

# Metal retention in geosynthetic clay liners following permeation by different mining solutions

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**ABSTRACT:** The leaching of hazardous metals and metalloids from mine tailings is a significant problem facing the mining industry. Although, in the past, geosynthetic clay liners (GCLs) have primarily been employed as leachate barriers in landfills, recent times have seen an increase in the variety of their applications, including applications in the mining industry. The capacity of GCLs to attenuate metals and metalloids (As, Al, Cd, Cu, Fe, Mn, Ni, Sr, Zn) from mine acidic rock drainage (ARD) water and a neutral-pH, As-rich water associated with gold mine tailings (GMT) was evaluated. Water-prehydrated GCLs were permeated with GMT and ARD for short (2 and 5 pore volumes, PV) and long (21 PV) periods. The long-term hydraulic conductivity of the GCLs increased from  $1.6 \times 10^{-11}$  m/s (water for 5 PV) to  $5.0 \times 10^{-11}$  m/s and  $1.3 \times 10^{-10}$  m/s after permeation with the GMT and ARD waters, respectively (21 PV). The distribution of metals within the GCL was quantified in order to differentiate between metals associated with precipitated compounds, soluble complexes in porewater, and sorbed metals. Metals sorbed to the GCL are reported in micrograms of metal per gram of bentonite (ppm), and are indicative of the GCL's sorption capacity for a barrier system. Significant differences existed between the soil tested at 2 PV, 5 PV and 21 PV. It was only at 5 PV that the precipitation of the ferrihydrite occurred in the ARD samples, and gypsum occurred in the GMT samples. These minerals were responsible for retention of metals in addition to the cation exchange of the GCL.

**KEYWORDS:** Geosynthetics, Geosynthetic clay liners, Metals, Bentonite, Attenuation, Sorption, Rock drainage, Mining

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## 1. INTRODUCTION

Metal and metalloid (hereafter referred to as metals) contamination from mine tailings is a priority problem facing the mining industry. Remediation efforts for tailings have centred on soil covers or sub-aqueous disposal, which reduce acid production and metal leaching by limiting infiltration and oxygen (Barbour 1990; Simms *et al.* 2000). Evidence that potentially toxic elements, particularly arsenic (As), may become mobile under these reducing conditions (Smedley and Kinniburgh 2002) reinforces the need for effective barriers. When dealing with some mine waste, it may be efficient to segregate the metal-rich material for separate disposal, in a lined

containment facility. The ease of mobility, low permeability and, more specifically, high attenuation capacity offered by the sodium-montmorillonite in GCLs suggests that they may be particularly beneficial for this type of application. The authors have previously reported research showing evidence of GCLs attenuating the metals present in landfill leachates and waters associated with acidic mine drainage (Lange *et al.* 2004). These experiments showed how the solution composition greatly affects the order of metal selectivity. In the design of such facilities it is necessary to have a mechanistic understanding of how metals become retained within a GCL barrier system when projecting the long-term fate of metals within the

GCL, as environmental factors such as pH and redox, which influence these mechanisms, may change over time.

Several field (case) studies have reported the use of GCLs at mine tailings sites (e.g. Olsta and Friedman 2002). This and other laboratory research often focuses on the mechanical properties of GCLs. There has been very little published research into the chemical changes occurring within the GCL when permeated with solutions containing metals and metalloids. Questions that concern metal interactions with GCLs are often answered using the data from sorption experiments with similar montmorillonite clay. For example, Weiss *et al.* (1998) treated a sodium montmorillonite with solutions containing various molar concentrations of Zn and Cd for the purpose of determining ion exchange equilibria. The large cation exchange capacity (CEC = 80–100 meq/100g) and surface area (800 m<sup>2</sup>/g) of sodium montmorillonites (Yong 2001) have been used to explain its considerable sorption of many metals (e.g. Li and Li 2001; Cooper *et al.* 2002; Abollino *et al.* 2003). Such metal ‘accounting’ information is often performed using single or equimolar multi-metal permeants. It is challenging to apply this information to a mine tailings model, as the presence of many cations (many with charges  $\geq 2$ ), complexing anions and ligands in typical mine waters often results in activities of metal ions in soil solution being different from what measured concentrations would suggest (McBride 1994). In cation exchange, or non-specific adsorption, the adsorbent shows some preference of ions, typically dependent on their valence ( $M^+ < M^{2+} < M^{3+}$ ) and degree of hydration. Metal uptake by soil is also limited by adsorption/desorption, precipitation/dissolution and complexation reactions: these phenomena are often treated as a continuum, because they are often difficult to distinguish from one another. Thermodynamic computer programs such as MINTEQ (Felmy *et al.* 1984) or PHREEQC (Parkhurst and Appelo 1999) can use a solubility approach to evaluate likely precipitates: this approach is sometimes limited to elements of high concentration, as research has shown that trace element concentrations are often lower than would be expected from the solubility product of likely precipitates (McBride 1994). For example, cation exchange may take up some of the metal, leaving the soil solution undersaturated for that species. Conversely, in soil solution, mineral surfaces may act to catalyse the nucleation step of crystallisation, reducing the extent of supersaturation necessary for precipitation to be initiated (e.g. smectites promoting gibbsite precipitation; McBride 1994). Other factors, such as the time restriction imposed by sorption and short column tests, may not allow for the development of minerals, and thus produce amorphous forms that have a higher solubility product, whereas crystalline forms are more thermodynamically stable and may not subsequently dissociate as easily. Selective sequential extraction (SSE) has been applied for the fractionation of solid phase associated elements in soils and sediments (Tessier *et al.* 1979; Lund 1990). Roehl and Czurda (1998) combined adsorption tests and chemical extraction to define the operational speciation of Cd and Pb sorbed to clays. This technique, however, becomes more susceptible to error as

the number of metals in solution increases and the selectivity of reagents towards solid materials becomes questionable. For this reason, and problems of inaccuracy due to operational inconsistency during extraction, solid–liquid phase separation, and re-adsorption, SSE has been termed ‘semi-quantitative’ or a ‘good qualitative indicator’ (Cabral and Lefebvre 1998). To a lesser extent anion exchange can also occur in montmorillonite through anion and ligand exchange.

As the soil/water interface in GCLs controls their hydraulic conductivity, researchers have monitored changes in hydraulic conductivity ( $k$ ) in the presence of various permeants. For example, Petrov *et al.* (1997) showed that  $k$  increases by 1.5–2 orders of magnitude as NaCl increases from 0.01 M to 2.0 M. The authors are not aware of any previous study that has investigated the interaction of GCLs with representative mine waters, although a few other studies are of relevance. In permeating a bentonite paste with ARD, Kashir and Yanful (2001) observed a fivefold increase in  $k$  after 23 PV and noted an acidic effluent of pH = 3 after only three pore volumes of flow. Kashir and Yanful noted ‘significant mineralogical alteration’ during this process, and showed how smectite was attacked owing to the narrowing of the smectite peak. Similarly, Ruhl and Daniel (1997) permeated a GCL with a strong acid (0.1 M HCl, pH = 1), which resulted in a  $k$  of  $3 \times 10^{-10}$  m/s (after 2.5 PV of permeation). These and other studies have suggested that as the pH drops, and more H<sup>+</sup>s occupy exchange sites, clay structures become unstable and dissolution may occur, causing short-circuiting and opened pore spaces (McBride 1994).

Yong (2001) demonstrated that assessment of the partitioning of metals in soils using solely effluent concentrations from soil column experiments, together with the application of mass balance calculations, can lead to error. Observation of the adsorption order of metals does not fully explain to what extent and how the metals are retarded or retained. Material investigation of the distribution of metals within the soil may act to help differentiate between metals associated with precipitation mechanisms, porewater soluble complexes, and actual sorbed metals.

The authors examined the attenuation of metals (As, Al, Cd, Cr, Cu, Fe, Mn, Ni, Sr, Zn) as contaminated water was permeated through GCLs. Specific attention is focused on waters associated with acidic rock drainage (ARD) and a neutral-pH, arsenic-rich solution typical of porewaters found in gold mine tailings (GMT). The paper seeks to examine the interaction of these waters with GCLs in terms of both the hydraulic conductivity and the change in the geochemical characteristics of the permeant (e.g. pH) with time. Following permeation, the distribution of metals within the GCL was quantified in position in the GCL and between the porewater and solid/soil phase.

## 2. MATERIALS

### 2.1. Geosynthetic clay liner

Tests were conducted using a thermally locked BENTOFIX™ NW GCL, which consisted of a scrip

reinforced-nonwoven carrier geotextile, and a nonwoven cover geotextile encapsulating a layer of granular Wyoming sodium bentonite (5500–6600 g bentonite/m<sup>2</sup>). The total cation exchange capacity, CEC (obtained using EPA method 9081; EPA 1986), was between 88 and 95 meq/100g. Rowe *et al.* (2000) analysed the properties of the granular bentonite and found it to consist of 91% smectite (montmorillonite), 5% quartz, 3% feldspar and 1% carbonate (GCL porewater pH = 8.1 to 8.6).

## 2.2. Synthetic (permeating) mine waters

Two permeant liquids representing mine waters documented from field activity were synthesised (Table 1). The first permeant represented a typical acid rock drainage water (ARD) with an elevated metal content and a high sulphate loading (pH ~ 3.3) (modified from Lange *et al.* 2004). The second permeant was a neutral-pH, arsenic-rich solution typical of porewaters found in gold mine tailings (GMT) (modified from Walker 2006, personal communication). The porewaters of gold mine tailings (upon which the GMT permeant was based) contain a low concentration of calcium relative to landfill leachate, which has been shown to increase the hydraulic conductivity of GCLs but has substantially more calcium than is observed in the ARD waters. The GMT also has a higher pH than acid rock drainage, which favours the co-precipitation/adsorption of a number of metals.

De-aired de-ionised water (DDW, pH = 6.9 to 7.1) was used for hydration and initial permeation of the GCL samples. In order to assess whether precipitates were thermodynamically stable once in contact with the GCL, the speciation program PHREEQC (Parkhurst and Appelo 1999) was used to calculate the saturation indices (SI).

## 3. METHOD

### 3.1. Water permeation and mine water permeation

Permeation was conducted using a rigid-wall permeameter ( $D = 54$  mm;  $H = 70.5$  mm) in which the normal stress was applied using a set of springs (applying 25 kPa of stress). This type of testing has previously been shown to be very effective for GCL–leachate compatibility studies (e.g. Petrov *et al.* 1997). All tests were performed in duplicate, yielding a total of six samples (two ARD, two GMT, two DDW).

The GCLs were hydrated with DDW for a period of 10 days. The samples were then permeated with 5 pore volumes (PV) of DDW in order to establish baseline conditions before the contaminated water was introduced. The gradient (and hence hydraulic conductivity,  $k$ ) was continuously monitored, and ranged from 600 to 1000 m/m. Analysis of the effluent geochemistry was conducted at regular intervals (typically every 3–5 days) for 30 cationic elements (using an inductively coupled plasma optical emission spectrometer: Varian, AX-Vista Pro CCD Simultaneous ICP-OES), pH and redox potential. Anions measured included total alkalinity (by titration) and Cl using an ion-specific electrode. Sulphate ( $\text{SO}_4^{2-}$ ) was calculated based on total S (S was fully oxidised).

### 3.2. Post-permeation GCL assays

Permeating GCLs with more than 20 PV of similar ARD water had previously led to the release of some metals at later stages of the test (Lange *et al.* 2004). Thus in this test series the GCL was examined at both early times (2 and 5 PV: i.e. prior to chemical equilibrium) and a later time (21 PV). Following permeation, the GCL samples were extruded from the fixed ring cells and carefully cut into pie-shaped sections and, given the small height of

**Table 1. Composition of permeant mining waters**

Parameter <sup>a</sup>	Gold mine tailings	Acid rock drainage	Units
Calcium ( $\text{Ca}^{2+}$ )	116	4.5	mg/l
Sodium ( $\text{Na}^+$ )	650	785	mg/l
Total sulphide ( $\text{S}_2^-$ ) <sup>b</sup>	502	1034	mg/l
Potassium ( $\text{K}^+$ )	11	667	mg/l
Magnesium ( $\text{Mg}^{2+}$ )	92	1	mg/l
Strontium ( $\text{Sr}^{2+}$ )	2.2	0.02	mg/l
Manganese ( $\text{Mn}^{2+}$ )	1.0	23	mg/l
Aluminium ( $\text{Al}^{3+}$ )	4.0	91	mg/l
Iron ( $\text{Fe}^{2+}$ )	1.2	218	mg/l
Copper ( $\text{Cu}^{2+}$ )	Nil	18	mg/l
Carbonate ( $\text{CO}_3^{2-}$ )	182	Nil	mg/l
Bicarbonate ( $\text{HCO}_3^-$ )	128	Nil	mg/l
Chloride ( $\text{Cl}^-$ )	219	1591	mg/l
Nitrate ( $\text{NO}_3^{2-}$ )	5	nil	mg/l
Cadmium ( $\text{Cd}^{2+}$ )	12.5	6.4	mg/l
Nickel ( $\text{Ni}^{2+}$ )	Nil	20	mg/l
Arsenic ( $\text{As}^{5+}$ )	4.5	2.5	mg/l
Zinc ( $\text{Zn}^{2+}$ )	Nil	102	mg/l
Redox potential	100	250	mV
pH	6.8	3.3	pH

<sup>a</sup>The valence indicated refers to how the ion was initially introduced.

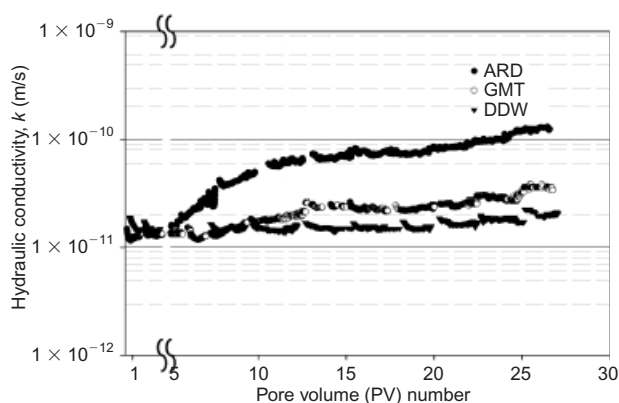
<sup>b</sup>Refers to total sulphide. Contaminants were introduced both as sulphates and as sulphides.

9.6 mm, into only two layers (upper and lower). The standard error, which incorporated the standard deviation between ICP measurements, dilution, and laboratory measurements, is shown on the relevant figures. The total soluble ions in the porewater were determined by shaking the 'wet' GCL section (geotextile intact, 1:10 soil to solution ratio) with 35 ml of DDW until the concentrations remained stable (12 h), and centrifuging. The supernatant was filtered and analysed by ICP-OES. This step often represents the first in selective chemical extraction to evaluate the 'soluble' or 'porewater' metals (Kaoser *et al.* 2005). Each soil layer was then subjected to aqua-regia soil digestion (Chen and Ma 2001), and the solution was analysed by ICP. The GCL materials were analysed by XRD (Philips X-Pert MPD, using copper tube). It should be noted that whereas the GCL bentonite was oven-dried at 100°C before aqua regia digestion, it was air-dried for XRD. It was important not to expose the XRD samples to temperatures above 100°C as this typically causes structural changes to the clay material. The mass balance between the total metals extracted by material analysis (i.e. porewater + soil) and the difference between the influent and effluent data was calculated. The upper layer refers to the top layer of the GCL (~4.8 mm) and the lower layer refers to the bottom layer of the GCL (~4.8 mm).

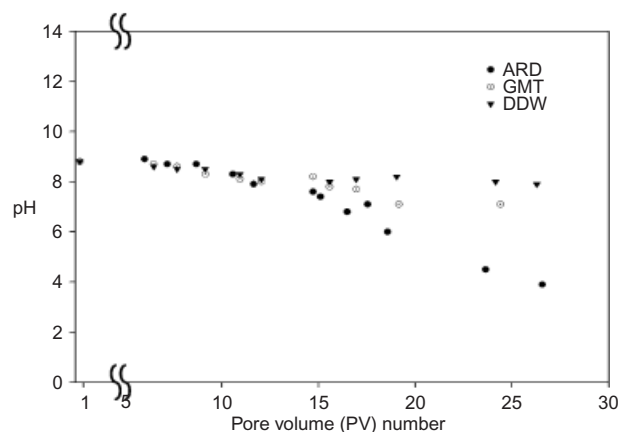
## 4. RESULTS

### 4.1. Hydraulic conductivity and pH

Figure 1 shows the average hydraulic conductivity data for both of the mine waters examined. The average hydraulic conductivity for DDW after 5 PV of permeation was  $1.6 \times 10^{-11}$  m/s, and rose to  $2.0 \times 10^{-11}$  m/s after 21 PV of permeation. For GCLs permeated with GMT and ARD the  $k$  values were  $1.7 \times 10^{-11}$  m/s and  $5.0 \times 10^{-11}$  m/s, respectively (averaged between two cells,  $R^2 = 0.95$ ), after ~5 PV of chemical permeation with mine waters, and  $3.5 \times 10^{-11}$  m/s and  $1.3 \times 10^{-10}$  m/s after 21 PV of permeation with mine waters. The pH of the GMT effluent (Figure 2) showed a very small decline in comparison with



**Figure 1.** GCL hydraulic conductivity for a GCL initially permeated with de-aired de-ionised water (5 PV DDW), followed by the mine waters, as a function of the number of pore volumes



**Figure 2.** pH change of permeant for a GCL initially permeated with de-aired, de-ionised water (5 PV DDW), followed by the mine waters, as a function of the number of pore volumes

the ARD effluent. In early times, several small increases in pH were observed notably for the ARD effluent waters, as cations such as Na and Ca resulted in temporary alkalinity contributions. Permeation by water caused a steady, yet small, decline in pH from 8.7 to 8.2.

Table 2 shows the effluent concentrations of the major cations, metals and chloride at selected pore volumes. Effluent from DDW permeation showed that Na and small amounts of other cations were being released. The metal concentrations in the effluent showed very significant attenuation (e.g.  $C/C_0 < 0.05$ ) at 2 PV for the GCL permeated with ARD; and at 5 PV, As, Ni, Al, Fe, Mn, Al, Cu and Zn had still not reached breakthrough (i.e.  $C/C_0 < 0.5$ , or half of the initial element's concentration). Cadmium was more mobile, reaching breakthrough at 3 PV. At 21 PV, Cu and Zn showed an increase above their influent values, indicating that a release from the soil was occurring. Furthermore, Fe and As in the ARD samples remained below their influent values for the duration of the test.

In the GMT tests, Cd reached breakthrough at 7.5 PV (later than ARD), and remained below its initial concentration throughout the test. The effluent data for As (GMT) were 'choppy'. It appeared to reach breakthrough at 8 PV, but declined significantly until 15 PV, where it began to increase again. Since this occurred in both samples, it was postulated that As was being controlled by multiple mechanisms (discussed in further detail later).

### 4.2. Acid rock drainage (ARD) permeated samples

Background or initial values referring to permeation with 5 PV of DDW are found in Figure 3. The total concentrations of the major cations and metals in the GCL samples permeated with ARD water after 2, 5 and 21 PV are shown in Figures 4 to 7. (Water permeation had a mild acidifying effect on the bentonite, as the effluent showed a small drop in pH, and small amounts of cations such as Na, Ca, Mg and K were released over 5 PV.)

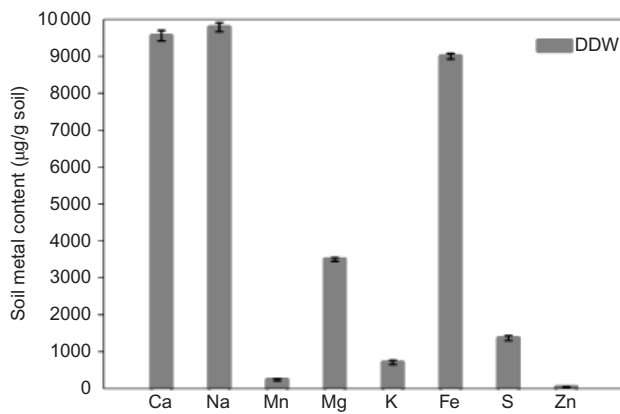
Metals associated with the porewater phase in the ARD samples typically consisted of only 1–5% of the total metals retained within the GCL. Significant uptake of all

**Table 2. Effluent concentrations of major cations, metals, and chloride**

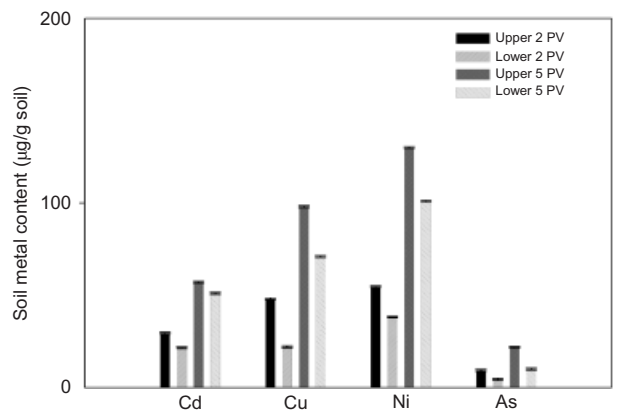
	Element <sup>a</sup>														
	Cd	Fe	Cu	Ni	Zn	As	Mg	Mn	Na	Cl	S	Ca	K	Al	Sr
DDW (water)															
1 PV	0	0	<0.1 <sup>b</sup>	0	0.3	0.15	0.4	0.01	383	54	96	3.6	5.6	7.8	<0.1
2 PV	0	<0.1	0	0	0.7	<0.1	0.46	0.02	283	35	37	5.6	10	6.5	0
5 PV	0	0.11	0	0	0.3	0.2	1.0	0.05	290	29	24	1.9	7	4.8	<0.1
ARD															
2 PV	0	0	0	0	0.3	0.2	0.9	0	374	433	267	153	8.4	5.7	<0.1
5 PV	4.0	0.2	0	3.4	44	0.2	20	6.6	1337	1251	878	126	193	4.5	1.4
8 PV	9.0	47	<0.05	11	96	0.1	29	17	1149	1853	973	202	399	6.4	1.8
10 PV	8.0	54	1.1	11	107	0.3	31	18	945	1711	1020	269	465	8.2	1.2
21 PV	6.0	170	19	19	120	1.9	17	22	819	1154	1045	225	605	19.9	1.1
GMT															
2 PV	0	0.2	n/a	n/a	n/a	0.6	0.83	<0.1	433	80	274	1.9	0.2	0.49	0.3
5 PV	3.5	0	n/a	n/a	n/a	1.1	2.4	1.3	557	126	416	79	0.3	1.0	0.7
8 PV	9.8	0.3	n/a	n/a	n/a	2.4	16	1.2	1189	242	374	197	0.5	1.2	0.5
10 PV	12	0.4	n/a	n/a	n/a	1.8	35	2.1	1251	248	950	203	1.8	0.90	1.76
21 PV	12	<0.1	n/a	n/a	n/a	4.1	56	2.4	1096	178	854	167	1.5	1.0	1.5

<sup>a</sup>Units in mg/l, measured from effluent porewaters.

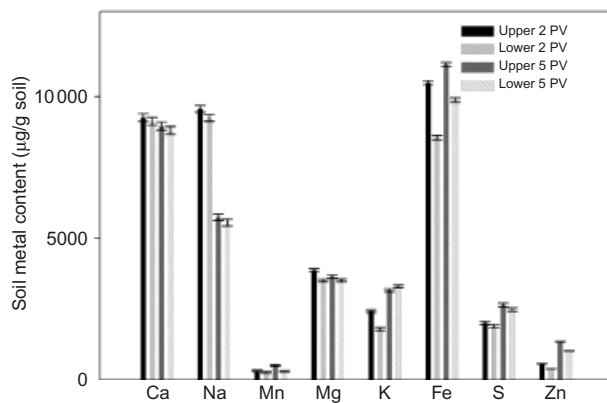
<sup>b</sup>Values less than 0.10 mg/l fall below the margin of error and are noted by <0.10 (mg/l).



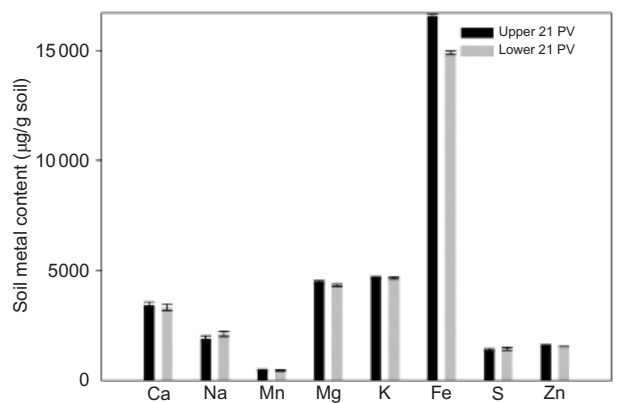
**Figure 3. Distribution of major cations and metals among upper and lower layer of DDW (background) permeated GCL samples (5 PV)**



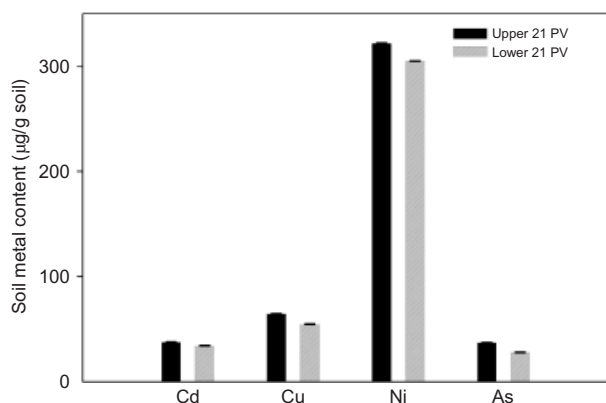
**Figure 5. Distribution of metals among upper and lower layer of ARD-permeated GCL samples at early times: 2 and 5 PV**



**Figure 4. Distribution of major cations and metals among upper and lower layer of ARD-permeated GCL samples at early times: 2 and 5 PV**



**Figure 6. Distribution of major cations and metals among upper and lower layer of ARD-permeated GCL samples at 21 PV**

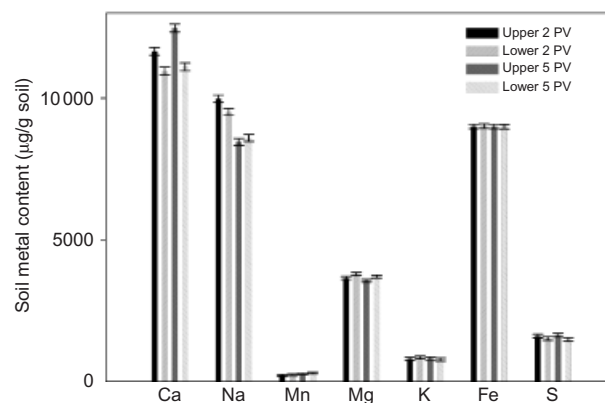


**Figure 7.** Distribution of metals among upper and lower layer of ARD-permeated GCL samples at 21 PV

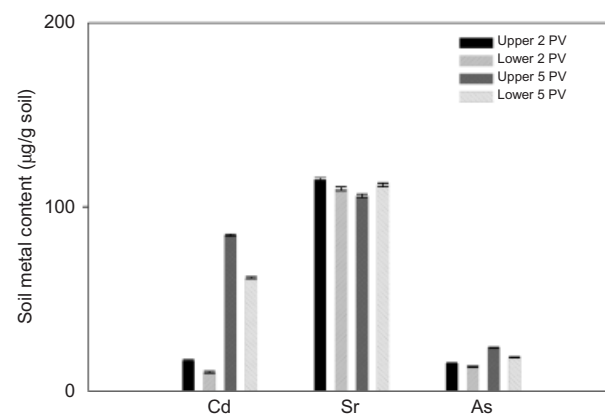
metals occurred at 2 PV and 5 PV, notably within the upper layer of the GCL. The accompaniment of considerable Na loss at 5 PV within the same layer showed that metals of greater charge were actively exchanging with Na, a common trend (Rowe *et al.* 2004). At 2 PV, Na concentrations temporarily increased, owing to the influx of Na addition. Co-precipitation of metals with Fe-Mn oxy-hydroxides, as evidenced by an orange-brown coloration on the upper layers and the measured high concentration of Fe, was probably responsible for additional metal retention, specifically for As (see discussion section). Repetitive XRD analysis of both wet and dry samples at 5 PV produced several new peaks, compatible with poorly crystalline ferrihydrite. At 21 PV the same orange coloration had migrated through the entire GCL's depth. Concentration effluent data showed some loss of Ca at 2 PV; however, significant depletion of Ca occurred between 5 PV and 21 PV. Calcite was found on the instrument and precipitating in the effluent bottle (XRD analysed), thereby making Ca effluent concentrations incorrect. In addition to cation exchange, this depletion was likely to have been the result of calcite dissolution (from the decrease in pH), as no measurable carbonate was found in the final samples. At 21 PV (Figures 6 and 7) As, Ni, Cd, Fe and Zn concentrations remained higher than at 5 PV. Conversely, Cu and Cd soil concentrations experienced a slight decrease in the soil (from 5 to 21 PV), coincident with the effluent measured release. At 21 PV the cationic concentrations in both layers approached an equivalence; however, they were still marginally larger in the upper layer. As this occurred following metal breakthrough and the drop in pH, these 'residual' concentrations may represent the fraction of metals that are more immobile and not as easily affected by changes in pH.

#### 4.3. Gold mine tailings water (GMT) permeated samples

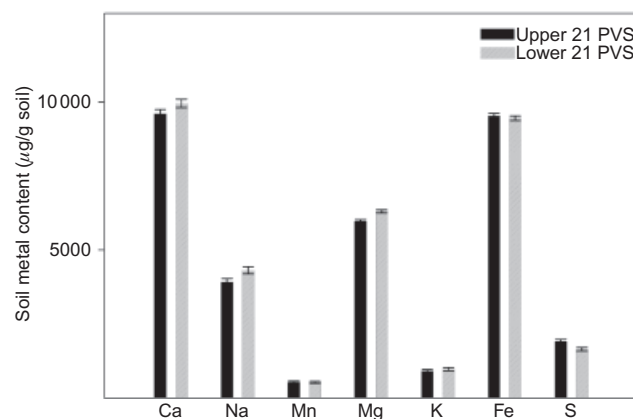
In the corresponding concentration–depth values for the GMT water permeated samples (Figures 8 to 11), Ca, Na and S concentrations were much higher than for the ARD samples at both 5 and 21 PV, and at both depths. The influent Na concentration and smaller metal loading (minimising exchange) mitigated its release. Gypsum was



**Figure 8.** Distribution of major cations and metals among upper and lower layer of GMT-permeated GCL samples at early times: 2 and 5 PV



**Figure 9.** Distribution of metals among upper and lower layer of GMT-permeated GCL samples at early times: 2 and 5 PV



**Figure 10.** Distribution of major cations and metals among upper and lower layers of GMT-permeated GCL samples at 21 pore volumes

identified by XRD ( $d = 7.63 \text{ \AA}$ ) in all GMT water-permeated samples at 5 PV, mainly in the GCL's upper layer, and in some samples (both layers) at 21 PV (Figure 12). This immobilised Ca and S to some extent. Cadmium showed superior attenuation than As at 5 PV; however, at 21 PV As attenuation markedly improved. Sr showed a mild, yet steady, increase in soil concentration over time, and was not accumulated more within one specific layer

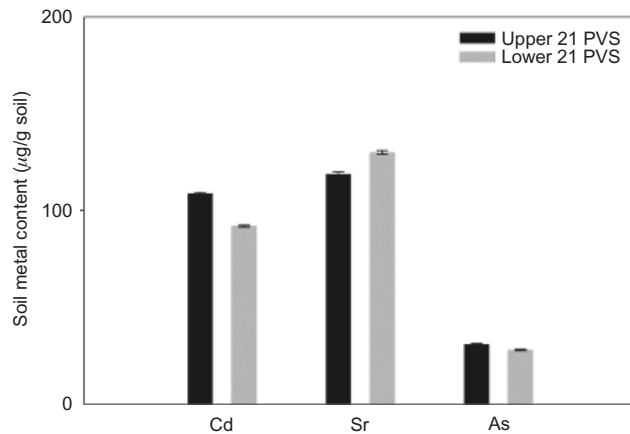


Figure 11. Distribution of metals among upper and lower layers of GMT-permeated GCL samples at 21 pore volumes

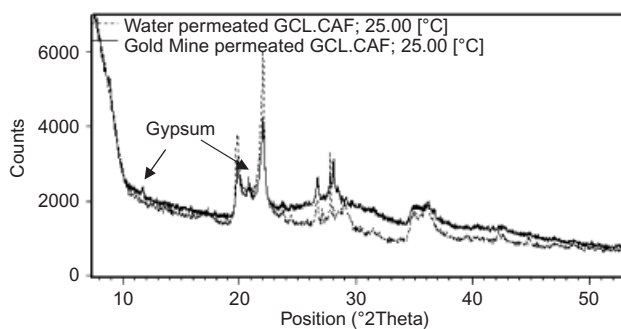


Figure 12. X-ray diffractogram of GCL bentonite following permeation with water and permeation with GMT

than another. Similar to the ARD, the percentage of total metals, including Cd, associated with the porewater phase ranged from 2% to 5% at 5 PV. One exception was arsenic (As), the porewater concentration of which accounted for 25–30% of total As retained in the GMT-permeated GCL samples at 5 PV. Figure 13 shows the relative amounts of As associated with (a) the porewater and (b) the soil phase.

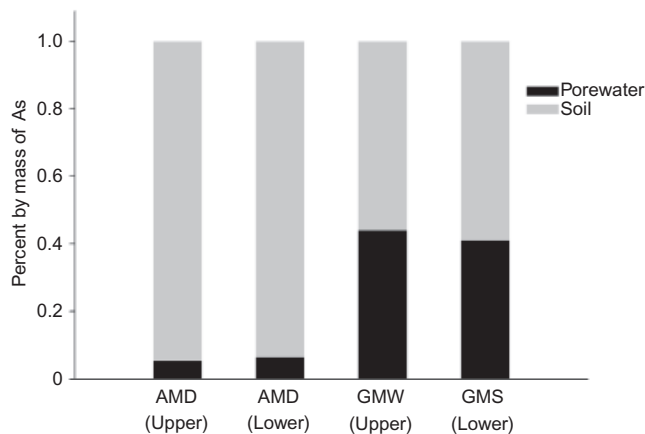


Figure 13. Distribution of (As) between the upper and lower layers of the GCL, and between the porewater and the sorbed soil for ARD and GMT samples at 5 pore volumes

## 5. DISCUSSION

GCLs were permeated with two typical, yet very different, mining waters, in order to (1) quantify the interaction of these waters with GCLs in terms of both the hydraulic conductivity and change in the geochemical characteristics of the permeant (e.g. pH) with time, and (2) assess the ability of GCLs to attenuate metals present in such waters. The different behaviour of the same metal in the different mining solutions tested demonstrated how the occurrence of multiple ionic species in solution can complicate the transport process, producing unanticipated chemical combinations due to opposing or collaborative effects. Analysis of the GCL material at different times not only allowed for the observation of metal associations, but proved valuable for reaffirming the retention of metals observed from prior monitoring of effluent data. Significant differences existed between the soil tested at 2 PV, 5 PV and 21 PV. It was only at 5 PV that the precipitation of the ferrihydrite occurred in the ARD samples, and gypsum occurred in the GMT samples. Although short-term tests at 2 PV showed significant results, the time and loading restrictions did not allow for the development of these minerals from amorphous (more soluble) forms. Crystalline forms of gypsum and ferrihydrite are more thermodynamically stable, and may not dissociate as easily, thus providing longer-term stability.

GCLs permeated with ARD and GMT waters showed a high retention capacity for all metals. Over the course of 21 PV the measured pH of the effluent from the ARD-permeated GCL samples reduced from 8.5 to 4.4 (influent 3.3), while the pH of the GMT only dropped to 7.1 (influent 6.8). The hydraulic conductivity of GCLs permeated with ARD increased by a factor of 3.0 at 5 PV and 8.0 at 21 PV. The hydraulic conductivity of the GMT samples at 5 PV was 1.1 times greater than that of water, and at 21 PV was 2.2 times greater. Depletion of Ca and Na was much higher for the ARD samples than for the GMT samples, mainly because of the higher metal loading and lower pH. The order of Na loss, followed by Ca, showed that metals were actively attenuating by cation exchange. The larger increase in hydraulic conductivity by the ARD samples resulted from the replacement of monovalent ions, specifically Na, by divalent and trivalent metals, causing the diffuse double layer to shrink and thus increasing the conducting pore space (similar to the findings of Ruhl and Daniel 1997). Metals sorbed by cation exchange to montmorillonite are not particularly influenced by small changes in pH and redox (Yong 2001); however, in increasingly acidic conditions  $H^+$  ions replace certain elements. Structural deterioration of the montmorillonite fraction could not be used to explain this increase, as XRD plots of the bentonite after 2, 5 and 21 PV of permeation maintained the montmorillonite peaks.

The significant accumulation of Fe oxyhydroxides in the ARD samples provided for additional and more permanent sorption for some metals. The point of zero net charge for ferric hydroxide typically occurs at a pH of 8, and it remains fairly insoluble until a pH of 5 (Evangelou 1998). Also oxides, such as Fe oxides, typically undergo

reductive dissolution at Eh values less than +100 mV and under more acidic conditions (Bennett and Dudas 2003).

At 5 PV effluent concentration data found the order of mobility of the metals to be:  $Cd > Zn > Mn > Ni > As > Fe > Cu$ . In fact, Cu is typically well known as one of the least mobile elements in most clay studies, theoretically attributed to its relative small hydrated radius of 0.21 nm (e.g. Yong 2001). However, at 21 PV a release of Cu from the soil (coincident with a pH decrease) was observed, while other metal concentrations such as Ni increased. Cd remained more mobile than the other metals at all times. In performing batch experiments with pure montmorillonite, Abollino *et al.* (2003) found similar results, and suggested that Cd sorption is hindered by the cation exchange mechanism at a lower pH, as its electrostatic attraction to the clay surface (larger radius and lower charge density) is hindered by the protonation of surface groups. They also attributed the decline of Cu sorption at low pH to its aquion's distorted geometry in increasingly acidic waters. This phenomenon reinforces the need to test with representative solutions, as it is difficult to translate accepted selectivity orders to the multiple species solutions of ARD or GMT used here.

Aluminium was well attenuated in the upper layers of the ARD samples. Aluminium is a compound commonly used in wastewater treatment because of its ability to quickly form low-solubility compounds (McBride 1994), and was identified by PHREEQC as a likely precipitate once in equilibrium with the GCL material (SI values slightly greater than 1 for many aluminium compounds such as boehmite (AlOOH) were calculated).

The authors had previously identified sulphide precipitates (Lange *et al.* 2004) responsible for metal retention in some landfill leachates; however, mining leachates are often much higher in Eh and have a higher sulphate content (e.g. Champagne *et al.* 2005), and, as a result, sulphates tend to dominate. In fact, metal sulphate complexes were identified in the PHREEQC results as one of the most predominant species. The greater retention of calcium and sulphate in the GMT samples, especially in the upper layer at 5 PVS, and then in both layers at 21 PV, was in part attributed to gypsum precipitation, as identified by XRD. Equilibrium calculations in PHREEQC for the GMT solution showed gypsum and calcite as having saturation indices (SI) of  $-0.62$  and  $-0.71$ , indicating the possibility for precipitation if concentrations of Ca were slightly increased (common ion effect), as it was during the experiments (contact with Ca from GCL soil and accumulation of Ca). The absence of gypsum within ARD samples may have resulted from the lower pH and lack of Ca from the influent water. Gypsum might also have been responsible in part for the retention of cadmium. Huang *et al.* (1999) showed how significant quantities of metals, especially Cd, can adsorb to gypsum during its crystal growth and nucleation. This may explain why Cd was much slower to be released into solution, and a considerable amount remained held within the soil. When compared with Cu in the ARD samples, Cu showed good sorption, but was released at a faster rate at a given pH, and its effluent value exceeded its influent value. Cu was

therefore sorbed to the surface of the clay/hydroxides but not incorporated into the structure.

Cadmium showed much stronger retention in the GMT samples than As at early times (2 and 5 PV). In fact, the large amount of As associated with the porewater phase in comparison with most metals, concentrations of which in the porewater constituted only 5% of the total metal content, indicated a lack of attenuation at 5 PV. Cadmium is a weakly hydrolysing metal and typically becomes sorbed at a higher pH, whereas As was probably excluded by competition with OH (arsenate form of  $H_2AsO_4^-$ ) or sulphate or general surface charge. Geochemical modelling suggests that arsenite ( $H_2AsO_3^-$ ) would have been the predominant species in the ARD leachate (owing to lower pH and Eh), and would sorb more strongly to the soil (Jain and Loeppert 2000). This is unlikely, however, as equilibrium was probably not reached during the length of this experiment in terms of arsenic speciation. Conversely, at 5 PV As was well attenuated by the ARD samples, most likely as a function of the Fe-oxyhydroxide surface attraction (a binuclear bridging mechanism) and lower pH. One might expect that sulphate would compete effectively with arsenate for sorption onto the Fe oxide surface, but McBride (1994) explains how arsenate can form a stronger oxy-anion ionic bond. At 21 PV, As sorption onto the GCLs increased in the GMT solution, a possible function of the lower pH. If the GMT effluent water were eventually to drop to its influent pH values, arsenic attenuation would be likely to increase, as the arsenate species became more retained at  $pH < 7.5$  (Jain and Loeppert 2000).

## 6. CONCLUSIONS

The GCL tested herein showed strong attenuation for a large number of metals and metalloids present in acid rock drainage (ARD) and neutral-pH gold mine waters. Material analysis, including metal porewater concentrations and metal distribution within the permeated GCLs, allowed the authors to gain insights into possible retention mechanisms at both early (100% sorption) and later times (approaching equilibrium). This information also confirmed the retention of metals observed from prior monitoring of effluent data. Analysis of the soil showed that precipitation of ferrihydrite (ARD) and gypsum (GMT) occurred only at 5 PV and not at early times (2 PV). These precipitates, being more thermodynamically stable than other amorphous forms, can have a significant impact on the behaviour of the contaminant transport process within the GCL. Several key factors may be identified from this research, as follows.

- Even though the GMT leachate had higher Ca than the ARD leachate, it proved to have less impact on the hydraulic conductivity and pH than the ARD (with no Ca content but acidic). Final  $k$  values of  $5 \times 10^{-11}$  m/s and  $1.3 \times 10^{-10}$  m/s were obtained after 21 PV of permeation with the GMT and ARD waters, respectively: still very low values. Over the course of 21 PV, the measured pH of the effluent

from the ARD-permeated GCL samples reduced from 8.5 to 4.4 (influent 3.3), while the pH of the GMT only dropped to 7.1 (influent 6.8).

- At 5 PV of ARD permeation, evidence of Fe-oxhydroxide precipitation occurred within the upper layers of the GCL, and showed a strong association with Zn, As, Cu and Ni. At 21 PV the Fe-oxhydroxide had migrated to nearly the entire depth of the GCL. Cu was affected by the drop in pH (ARD), showing a slight release from the soil at 21 PV. Cd remained more mobile than the other metals, experiencing earlier breakthrough times and smaller soil concentrations.
- The concentrations for each cation and metal became more evenly distributed between the upper and lower layers of the GCL (at 21 PV) for the ARD. As this occurred following metal breakthrough and the drop in pH, these 'residual' concentrations may represent the fraction of metals that are more immobile and not as easily affected by changes in pH. These concentrations, in ppm, are: As = 37, Cd = 41, Cu = 66, Fe = 15000, Mn = 380, Ni = 320, Zn = 1900.
- Gypsum precipitation (XRD identified) occurred in the GMT samples, was responsible for Ca and S attenuation, and could have been responsible for Cd and As attenuation.
- Cd showed much stronger retention in the GMT samples than As. In fact, the large amount of As associated with the porewater phase in comparison with most metals, concentrations of which in the porewater constituted only 5% of the total metal content, indicated a lack of attenuation at 5 PV. The porewater concentration of As accounted for 20–30% of total As retained in the GMT samples, while typical metals associated with the porewater phase consisted of only 1–2% of the total metals retained within the GCL. Cd is a weakly hydrolysing metal and typically becomes sorbed at a higher pH, whereas As is likely to have been disfavoured by competition with OH (arsenate form of  $\text{H}_2\text{AsO}_4^-$ ) or sulphate or general surface charge. At 21 PV As attenuation improved to that of Cd.
- The testing herein assumed the permeant to be in direct contact with the GCL, and used very conservative values for the metal loading design of the leachates (close to maximum reported values). In field applications with less metal loading, GCLs would be expected to provide even better retardation than observed here. This research shows how GCLs have the capability to retard the movement of metals; however, it is necessary to know the solution composition and give special attention to more mobile metals such as Cd. GCLs would be particularly suitable for short-term containment (i.e. holding ponds) of both ARD and GMT. Although GCLs show promise for long-term (i.e. permanent) containment, more compatibility (i.e.  $k$  testing) and geochemical analyses need to be undertaken for longer periods in the laboratory. In predicting the

long-term performance of the GCL, it is important to examine the mechanism of metal attenuation, such as the role of adsorption onto bentonite, sorption onto Fe and Mn hydroxides, and the effect of reducing conditions on the long-term stability of these hydroxides.

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## NOTATIONS

Basic SI units are given in parentheses.

$k$  hydraulic conductivity (m/s)

## ABBREVIATIONS

ARD	acid rock drainage
CEC	cation exchange capacity
DDW	de-aired de-ionised water
GCL	geosynthetic clay liner
GMT	gold mine tailings
PV	pore volume
SI	saturation index
SSE	selective sequential extraction
XRD	X-ray diffraction

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