



The potential role of geosynthetic clay liners in mine water treatment systems

K. Lange¹, R.K. Rowe*, H. Jamieson²

GeoEngineering Centre at Queen's-RMC, Queen's University, Kingston, Ontario, CA K7L 3N6, Canada

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ABSTRACT

Combined passive treatment technologies have been used to treat acidic rock drainage (ARD), the well-known acute and costly environmental problem facing the mining industry. It is shown that geosynthetic clay liners (GCLs) were able to attenuate metals from lime treated ARD water, and maintain a neutral pH and low hydraulic conductivity (less than 4.0×10^{-11} m/s) after 16 pore volumes of permeation; this implies their usefulness as a potentially significant component in combined passive treatment systems. Presented are laboratory breakthrough data for Cu, Cd, Ni, Mn, and Zn from the permeation of GCLs with 16 pore volumes of ARD, treated ARD (TARD), and a landfill leachate. Metal retention occurred in all solutions, but was greatest for the TARD, producing removal efficiencies of greater than 80%.

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1. Introduction

Different methods have been developed to treat, isolate, and minimize the runoff associated with acidic rock drainage (ARD), the low pH waters resulting from contact between sulfidic minerals (e.g. pyrite) with water and oxygen, which is often associated with high metal concentrations and distinctive red-stained waters. Modern mines incorporate preventative technologies to limit ARD that may include isolation of mine tailings from oxygen by using covers or sub-aqueous disposal methods. A serious concern of regulatory agencies, however, is that they will discover ARD after mine closure and abandonment when financial resources to fund mitigation are no longer available (Norman and Raforth, 1998). In Canada, there are approximately 10,000 inactive mines with little information on the total number, size, and impacts on water quantity and quality (Environment Canada, 2004; National Orphaned/Abandoned Mines Initiative).

Conventional effluent treatment typically involves adding alkalinity to the water to raise the pH and produce metal-rich precipitates which are settled and filtered out. The high cost associated with the operation and maintenance of such systems has

prompted an increased use of passive treatment technologies. For some metals, leaching may only be significant if the pH drops below 5.5–6; however, this is not true for elements like molybdenum, manganese, zinc, cadmium, and arsenic that can remain soluble at pH values near and greater than 7 (e.g. Sibrell et al., 2007).

Liner materials are needed at different stages in a treatment system to minimize the downward flux of the metal and metalloids contaminants. Geosynthetic clay liners (GCLs) have been widely used in containment applications as part of composite liners for landfills (e.g. Brachman and Gudina, 2008; Bouazza et al., 2008) and more recent research has shown that they are effective in attenuating metals from some mining leachates (e.g. Lange et al., 2007). However, they have not been widely used for containment of ARD or ARD that has been treated with a chemical such as lime to raise the pH. This present research examines the potential use of GCLs to serve as a barrier component in combined passive treatment systems of ARD waters. Geosynthetic clay liners could be particularly useful in such an environment as they maintain a low hydraulic conductivity over a range of conditions, possess a high unit attenuation capacity, and have an ease of mobility often required in remote mining locations, where local clay is often not available. The results of this study differ from those contained in Lange et al. (2007) by examining the potential use of GCLs in passive mine treatment, where shorter containment times would occur, and the contained solution would have low metals concentration.

While chemical treatment or some other form of active effluent treatment has traditionally been conducted in Canada (e.g. Banks et al., 1997; Zinck and Aube, 2000), recently, greater consideration

* Corresponding author. Tel.: +1 613 533 6933; fax: +1 613 533 2128.

E-mail addresses: langekarina@hotmail.com (K. Lange), kerry@civil.queensu.ca (R.K. Rowe), jamieson@geol.queensu.ca (H. Jamieson).

¹ Tel.: +1 613 533 6000x78227; fax: +1 613 533 2128.

² Tel.: +1 613 533 6181; fax: +1 613 533 6592.

has been given to forms of passive treatment; or at least the combination of active and passive treatment (Sheoran and Sheoran, 2006). Components of passive treatment are increasingly being incorporated into conventionally engineered systems (e.g. Kalin, 2004). Since the 1980s, field research has shown that passive technologies, which consist of natural or constructed wetlands and bogs, are capable of lowering metal concentrations and increasing the pH of mine effluents (Younger et al., 2002; Johnson and Hallberg, 2002). Research in this area is rapidly growing including studies involving 'geomicrobiology' (Kalin, 2004), which focuses on the bacteria and ecological effects of passive treatment. However, some research has shown that 'isolated' passive treatment systems, which rely on natural chemical and biological processes to remediate ARD, may be susceptible to failure (Johnson and Hallberg, 2002). For example, Barton and Karathanasis (1999) renovated a failed surface aerobic wetland by the incorporation of limestone drains and a series of successive alkalinity production systems. Hence passive treatment systems are being combined with active components (e.g. addition of lime) to tailor to the needs of the level of treatment required (e.g. Champagne et al., 2005).

Two common methods for passive treatment discussed are aerobic and anaerobic. In passive anaerobic treatment, bacterial reduction of sulfate and iron, and the precipitation of metal sulfides are important (e.g. Chen and Li, 2007). This research focuses on surface, or aerobic treatments, where the dominant process is oxidation of metals followed by precipitation of their hydroxides. For aerobic wetlands, the water must be kept sufficiently alkaline – this can involve either lime addition and mixing or the installation of an anoxic limestone drain (trench filled with crushed limestone). A constructed pond or wetland is located to receive the ARD, where it is expected to undergo metal removal and neutralization (Sheoran and Sheoran, 2006).

Since the minimum hydroxide solubilities for the different metals occur at different pH values, maximum removal efficiency of mixed metals can only be achieved at a certain (high) pH level (e.g. Feng et al., 2000). Fig. 1 plots the minimal metal concentrations needed to maintain equilibrium with their respective hydroxide phases versus pH. To reach a given metal concentration such as 10^{-4} , Zn hydroxides precipitate at a pH of 8, but the pH needs to be raised to effectively precipitate other metals such as Cd (indicated by arrows on Fig. 1).

Feng et al. (2000) treated an ARD (TARD) of pH 1.65 with successive levels of lime up to a pH of 12.50. At a pH of 5.70, metals such as Cu, Fe, Mn, Ni, Sr, Zn, and Cd were significantly reduced (see

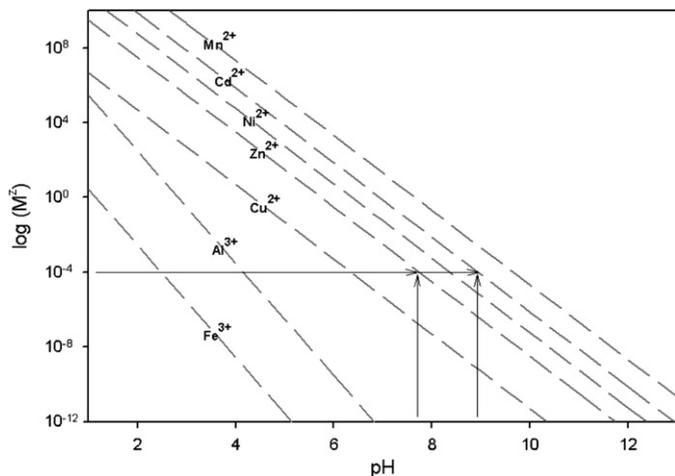


Fig. 1. Graph of metal concentration (M , metal; z , valence) in solution (versus pH) to maintain equilibrium with solid hydroxide.

TARD in Table 1); however they still remained at levels above effluent standards. Other authors have shown similar results. For example, Champagne et al. (2005) showed that Cd only experienced a 66.5% removal rate from a combined passive system in comparison to other metals such as Fe, Al and Zn that had greater than 99% removal efficiencies. Therefore, barriers capable of attenuating the remaining dissolved metals, such as Cd, are needed to minimize the downward flux of metal contaminants, specifically in holding ponds where detention times may be lengthy.

To that end, this research assessed the potential of GCLs for attenuating the metals from a treated ARD effluent. The objectives of this study were to: (1) evaluate the GCL's capacity to retain metals from TARD and ARD waters by permeation testing; (2) monitor the hydraulic conductivity of the GCL during permeation; and (3) compare the measured GCL properties (from 1 and 2) with those of a typical landfill leachate.

2. Materials

2.1. Permeant solutions

This study tested three solutions: acidic rock drainage (ARD), treated acidic rock drainage (TARD) and a landfill leachate (LL). The composition of each solution is found in Table 1. A synthetic ARD solution was prepared that consisted of a high metal and sulfate loading with a low pH (~ 3). The ARD composition was based on a synthetic ARD used by Champagne et al. (2005) which simulated measured ARD samples from several abandoned mine sites.

For the TARD, actual ARD was treated with calcium hydroxide by CANMET laboratories (Mining and Mineral Sciences, Ottawa). The resulting hydroxide ion had raised the pH ($\text{Ca}[\text{OH}]_2(\text{s}) \rightarrow \text{Ca}^{2+} + 2\text{OH}^-$) and combined with metals (M) in ARD solution to precipitate soluble hydroxides ($M^{n+} + \text{OH}^- \rightarrow M[\text{OH}]^n(\text{s})$). The filtered supernatant TARD had a pH of 6.4. In order to simulate a TARD closer to that of Feng et al. (2000) (Table 1) the solution was

Table 1
Composition of mine waters.

Dissolved constituent (mg/L)	ARD	TARD ^a	Feng et al. (2000)	Landfill leachate (LL)	Gold mine waste water (GMW)
Cl	1700	300	673	4100	270
Al	90	3.4	139	10	4
As	2.53	0.29	n/a	1	4.5
Ca	4.61	365	641	700	116
Cu	14	5	1.04	3	0.1
Cd	41	12	0.24	2.5	7
Fe	218	10	578	12	10
K	400	8	n/a	190	8
Mg	1	45	352	244	92
Mn	19	6	106	14	6
Ni	19	6	5.03	5	–
SO ₄	3102	1440	4330	75	1890
Sr	0.1	0.5	1.39	12	0.5
Zn	128	8	5.67	110	–
Na	789	340	n/a	2300	665
NH ₄	–	–	–	413	6
PO ₄	–	–	–	16	–
NO ₃	–	–	–	29	6
Urea CO(NH ₂) ₂	–	–	–	300	–
HCO ₃ + CO ₃	–	–	–	2800	–
Acetic acid	–	–	–	7340	–
Propionic acid	–	–	–	4970	–
Butyric acid	–	–	–	959	–
Eh (mV)	348	154	Unknown	80	198
pH	2.6	5.8	5.7	5.0	6.8

^a Treated with $\text{Ca}(\text{OH})_2$

spiked with metal sulfate salts. This raised the concentrations of Fe, Cd, Ni, and Zn, and decreased the pH to 5.8.

Laboratory-synthesized landfill leachate (LL) was created with a combination of metal salts, inorganic acids and urea in an attempt to simulate leachate from municipal solid waste during the early anaerobic degradation phase, where acid fermentation causes a decrease in pH, and where metal mobility is typically highest (e.g. Urase et al., 1997). In Section 5, this study also draws on permeation data from Lange et al. (2007), where a solution typical of those found with carbonate-associated gold mine tailings was used to permeate GCLs in a similar manner to this study. The gold mine tailings water (GMW) has a near neutral pH with metal concentrations of 4.5 and 7 ppm for As and Cd respectively.

Metal determinations for all waters in this study were performed with a Varian Inductively Coupled Plasma Atomic Spectrometer (ICP-AES). Chloride content was measured with an ion specific electrode, and sulfate concentrations were calculated based on total sulfur content. The distribution of metal aqueous species and SI indices of minerals in equilibrium with the solution compositions were calculated using PHREEQC (Parkhurst and Appelo, 1999); all SI indices were less than 1, and no visible precipitate in the solutions were observed.

2.2. GCL tested

The GCL tested in this study was a BENTOFIX™ NWL GCL (Terraflix Geosynthetics Inc., Ontario, Canada) and consisted of a nonwoven carrier geotextile, a layer of granular Wyoming sodium bentonite and a nonwoven cover geotextile needlepunched together with the fibers thermally treated on the carrier geotextile. The most recent characterization of the GCL bentonite by X-ray diffraction (XRD) is from Lange et al. (in press) which yielded the following quantitative analysis: 77% smectite (montmorillonite), 8% plagioclase, approximately 5% each of cristobalite and quartz and trace amounts of illite, mica, calcite, pyrite and clinoptilolite (a zeolite). An extensive mineralogical study of eight bentonites has been conducted by Guyonnet et al. (2009) who highlighted the variety of composition of GCL bentonites.

The procedure used to prepare the GCL specimens for permeation with the fixed wall (FW) permeameter was similar to that described by Petrov et al. (1997). A water-wetted steel cutting shoe was placed on the cover geotextile of the GCL, and slowly forced through the GCL specimen with a hand lever assembly. The average mass (dry) per unit area of the GCL was 4720 g/m².

3. Methods

3.1. Permeation testing

The GCLs were permeated with ARD, TARD and LL solutions using the fixed wall (FW) permeameter designed by Fernandez (1989), where a constant flow rate of 3.1 mL per day was applied. The FW permeameter consists of a stainless steel cell (diameter of 54 mm and a height of 70.5 mm) where the cut GCL is encapsulated between an upper and lower porous stone. A low static confining stress (25 kPa) was applied directly to the top of the specimen by springs sandwiched between locator caps. The GCLs were first hydrated under static head, and then were permeated with five pore volumes (PV) of DDW in order to establish baseline conditions before the contaminated water was introduced. During the first 1–4 PV of permeation, Na and small amounts of other ions were measured in the effluent. It should be noted that the laboratory DDW was slightly acidic (e.g. pH 6.8), which may have resulted in a slightly greater release of ions than would be expected from a neutral water. Following DDW permeation, 16 PV of the respective

solutions were passed through the GCL. The gradient (and hence hydraulic conductivity, k) was continuously monitored, and ranged from 600 to 1000 m/m. Effluent waters were analyzed for pH, Cl and cationic content over time. Two GCL samples were tested for each solution for quality control (total of six), and at 10 PV, one GCL from each solution was extruded and tested for retained metal concentrations.

3.2. Soil digestion

Following solution permeation, the GCLs were removed from the cells, dried under vacuum, and were digested by the aqua-regia method (e.g. Chen and Ma, 2001). The solution was analyzed for cationic content by ICP-AES, as explained above. In previous study by the authors, portions of the GCL were used for other analysis such as porewater, XRD, etc., leaving only a fraction for soil digestion. In an attempt to minimize error, this study maximized the digestion of the sample by digesting the majority (about 95%) of the GCL; the other 5% was used for analysis related to a different study.

4. Results

4.1. Hydraulic conductivity

The hydraulic conductivity (k) over time for the three tested solutions, along with the GMW and DDW for comparison, are shown in Fig. 2 as a function of PV. Each curve represents the average of two test cells (up to 10 PV). Measurements between each set of test cells were very close in value, exhibiting an R^2 of greater than, or equal to, 95%. From 10 PV to 16 PV the data is from one cell. Initial permeation with 5 PV of DDW resulted in an average k value (average of four tests, i.e. eight cells) of 1.4×10^{-11} m/s (standard deviation = 0.2×10^{-11}). Permeation continued for a total of 16 PV (total of 21 PV) until the LL cells developed a black bacteria (and odour) in the effluent port that warranted test termination; this was considered acceptable as the extent of retardation for all metals had been assessed, and the hydraulic conductivity for the TARD had been constant for the at least 6 PV of measurement (authors such as Lange et al. (2007) have performed ARD permeation tests for longer time periods). After permeation with 16 PV of solution (total of 21 PV), the k of the permeants was as follows (from largest to smallest): ARD = 7.5×10^{-11} m/s; TARD = 3.5×10^{-11} ; LL = 4.4×10^{-11} m/s; and GMW = 2.5×10^{-11} m/s.

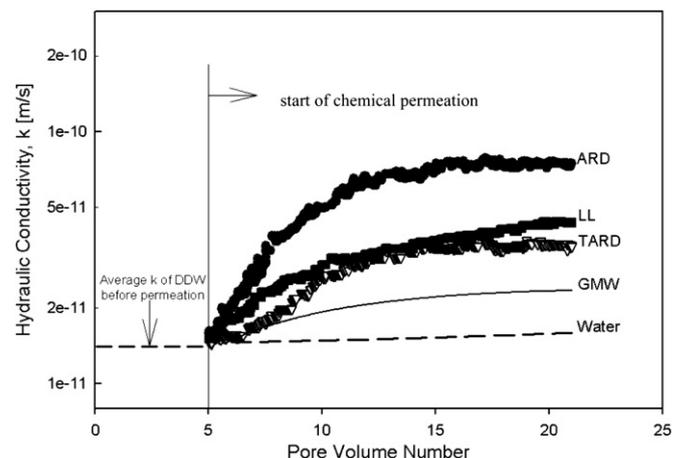


Fig. 2. Hydraulic conductivity plotted as a function of pore volume number for ARD, TARD and LL solutions. Solid lines represent the average hydraulic conductivity of GMW and DDW from another study by Lange et al. (2007).

4.2. Metal transport

Normalized concentration data (where the effluent concentration C , is divided by the permeant initial concentration, C_0) for the metals Cd, Cu, Mn, Ni, Zn and for Cl over time (i.e. breakthrough curves) from the effluent sample port of the FW apparatus for the ARD and TARD waters are shown in Fig. 3. Concentrations of Fe and K in the TARD were initially very low and were not measurable in effluent waters, and are therefore not shown in the data set. Measurements of Fe and K attenuation over time for the ARD can be found in Lange et al. (2007). Chloride reached breakthrough shortly after 3 PV. The 50% breakthrough line is highlighted in the figures (thus the breakthrough time is taken to correspond to when $C/C_0 = 0.5$). When the chemical solutions were first inserted into the apparatus, residual DDW remained in the steel tubing and test cell. Therefore, an initial dilution of the chemical solution would have occurred, causing breakthrough to be delayed by one or two pore volumes. Nonetheless, the research focuses on the retardation of metals in the GCL, and focuses on the difference in breakthrough between Cl, a conservative tracer, and the metals.

Larger breakthrough times were exhibited by all metals from the TARD waters compared with the ARD. For example, breakthrough of Mn in the TARD occurred at 10.5 PV and at 6.5 PV for the ARD. The order of attenuation was very similar between the two waters, following the order (from most to least attenuated): Cu > Ni > Zn > Cd > Mn; however Cd and Zn had essential the same profiles in the ARD while Zn was more attenuated than Cd from the TARD water. Cadmium data for the ARD and TARD waters is compared with those of LL and GM in Fig. 4. The Cd plots for the ARD and LL waters were similar and experienced earlier breakthrough times than those of the GM and TARD. A summary of metal breakthrough times for the three tested solutions (ARD, TARD and LL) is given in Table 2.

Sodium, SO_4 and pH effluent data for ARD, TARD, and LL are shown in Fig. 5; despite their very different initial concentrations, concentration–time curves for Na and SO_4 were very similar. After permeation with 16 PV of TARD, the pH of the effluent waters dropped from 8.3 (average pH of effluent after 5 PV of DDW permeation) to 6.0 (influent TARD pH = 5–5.8) and the pH of the ARD effluent waters dropped to 4.2. Lange et al. (2007) noted a delay in SO_4 breakthrough for the GMW solution, and attributed it to gypsum precipitation; however that did not occur for the ARD, LL and TARD during this experiment, where SO_4 breakthrough occurred near to that of Cl.

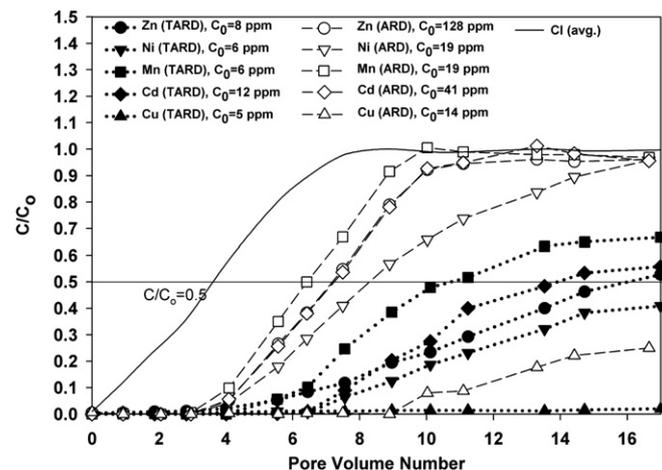


Fig. 3. Normalized concentration of Cd, Cu, Mn, Ni, Zn, and average Cl versus pore volume number for TARD and ARD waters. Breakthrough line is shown.

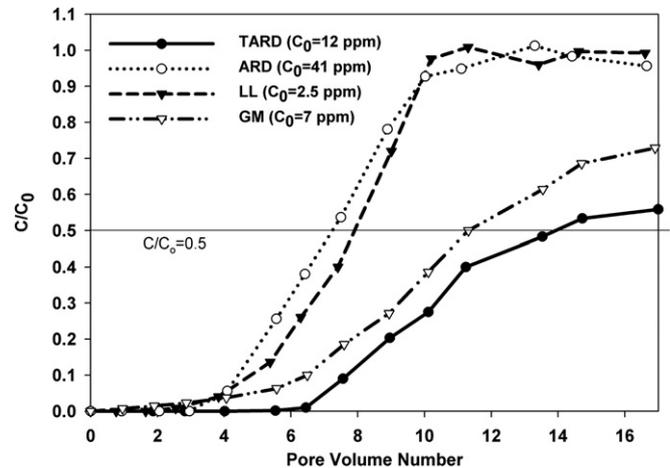


Fig. 4. Normalized concentration of Cd versus pore volume number for TARD, ARD, LL and GMW. Breakthrough line is shown.

The corresponding total mass retained for the plotted cations and anions for all solutions is shown in Table 3. Also shown is the difference between the measured cation content by soil digestion and the inferred percent retention by subtracting the effluent from the influent concentration(s). Nickel, Cu, Zn, and Cd showed greater than 80% removal efficiencies from the TARD solution after 16 pore volumes of GCL water permeation (Mn had a removal efficiency of 73%). Despite having a higher pH than the ARD, metals in the LL were sorbed at percentages very similar to those in the ARD (Ni sorption in LL = 56% and ARD = 52%). The largest Na loss occurred in the ARD; this has previously been explained by the larger metal and hydrogen loading compared with other solutions (Lange et al., 2007). The ARD exhibited a significant loss in Ca (–3729 $\mu\text{g/g}$ bentonite), likely due to cation exchange and the dissolution of Ca-minerals such as calcite when in contact with low pH water. A small Ca loss was noted in the LL (–465 $\mu\text{g/g}$ bentonite), while Ca was attenuated within the TARD waters (+6239 $\mu\text{g/g}$ bentonite). Most soil digestion measurements were within 10% of the inferred value, with the exception of Mn (ARD, TARD), Na (TARD) and Ca (LL). The error associated with Na is likely from it being the primary exchange ion in the Wyoming bentonite and tending to vary in initial content; the Ca levels may have fluctuated due to the dissolution of some Ca-bearing minerals in the GCL bentonite.

5. Discussion

Attenuation of the metals Cu, Cd, Mn, Ni, Zn, in the GCL was significantly higher for the treated ARD (TARD) water compared with the untreated ARD. Specifically, metals that have been shown to be more difficult to precipitate by lime treatment such as Ni, Zn, and Cd, showed greater than 80% removal efficiencies from the TARD solution after 16 pore volumes of water permeation.

Table 2
Pore volume at metal breakthrough ($C/C_0 = 0.5$).

Metal	ARD	TARD	LL
Cu	nr	nr	nr
Cd	7	13.8	8.0
Mn	6.4	10.5	5.6
Ni	8.4	nr	7.0
Zn	7	15.9	6.8
Cl	4	3.7	3.6

nr, did not reach breakthrough.

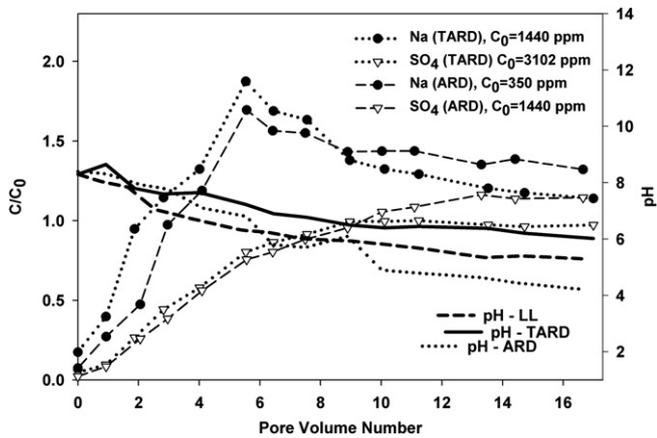


Fig. 5. Normalized concentration of Na, and SO_4 versus pore volume number (left axis) and pH (right axis) for TARD and ARD waters.

Consistent with other research, the greater sorption of metals in the TARD compared with the ARD is attributed to pH (e.g. House, 1998) where the hydroxylated metal cations from the TARD (e.g. CuOH^+) were preferentially sorbed with respect to free cations that existed in the lower pH ARD water (e.g. Cu^{2+}). In fact, Ni, Cd and Zn in the TARD did not reach their initial concentrations by the end of the test; for ARD, the same metals reached initial concentrations, and in one case reached concentrations above initial values due to desorption. During ARD permeation, the pH decreased over time, and several mechanisms could have attributed to the decreased sorption (and release) of metals, including the increased competition from H^+ ions with metals for attachment sites and the loss of negative charge of edge and oxide sites to which certain metals are often preferentially sorbed (e.g. Jackson, 1998). The partly covalent surface complex that often forms between the metals with the edge

sites and oxides in clays is stronger than the loose electrostatic binding to the 001 faces (interlayer sorption), and more opportunity for this type of bonding would exist in the more alkaline environment of the TARD. Cadmium was desorbed slightly from the ARD sample; this was likely due to displacement by a competing cation or by dissolution of a mineral with a high solubility (e.g. carbonate) to which it was attached. In previous research, Lange et al. (2007) noted the precipitation of Fe oxides in the ARD waters. The concentrations of Fe and other metals in the TARD were much lower than in the ARD, and therefore precipitation mechanisms, specifically involving Fe, were not likely the principal control for attenuation in the TARD. In a series of diffusion tests using similar solutions conducted by Lange et al. (2009), the extrapolated K_d (distribution coefficient) value was notably higher for the TARD than for other solutions. The diffusion tests monitored the migration of metals and other cations from a source cell through the GCL to a receptor cell, and for the TARD waters, very low values for metals were observed in the receptor over time in comparison to those observed for the ARD cell. For example, at 40 days, the receptor Cd concentration of the ARD and TARD were 3.5 mg/L and 0.1 mg/L respectively.

Although the LL solution was 2 pH units higher than the ARD, the metal breakthrough curves of the LL and ARD were very similar. For LL, the Cl loading was very high in comparison to the other solutions; other anions in the LL (that were not present in the ARD), such as carbonate, have been known to complex with metals, and possibly inhibit sorption (e.g. Jackson, 1998). While it appears that pH may be important, the effect of complexing cations can also be significant.

The application of constant flow rate testing allowed for a large volume of solution to be passed through the GCL. For example, one pore volume took approximately 7 days to pass through the GCL. After permeation with 16 PV of solution (total of 21 PV), the final k of the ARD permeated GCL was twice as large as the TARD permeated GCL (3.5×10^{-11} m/s and 7.5×10^{-11} m/s respectively); both still very low values. The values are consistent with some of the lower k

Table 3
Calculated and predicted percent of metal retention in digested GCL soils.

Constituent	Total mass in (Mg)	Total mass out (mg)	Calculated mass (μg) retained per gram soil (mass in – mass out)	Measured metal (digested) mass (μg) retained per gram soil	Fraction retained ^a	Difference (%) ^b
TARD						
Cu	1.53	0.018	151	158	1.03	4.3
Cd	3.67	0.90	277	292	0.80	5.2
Mn	1.84	0.63	120	134	0.73	10.4
Ni	1.83	0.21	162	170	0.93	4.7
Zn	2.44	0.56	188	194	0.80	3.0
SO_4^{2-}	441	356	8454	8564	0.19	1.3
Na	107	137	–3031	–2719	–0.25	–11.5
Ca	112	52	5983	6239	0.56	4.1
ARD						
Cu	4.19	0.35	385	375	0.89	–2.5
Cd	12.3	7.35	494	516	0.42	4.0
Mn	5.69	3.64	205	235	0.41	12.8
Ni	5.69	2.84	285	296	0.52	3.6
Zn	38.4	22.7	1566	1606	0.42	2.5
SO_4^{2-}	930	812	11814	13064	0.14	9.6
Na	237	301	–6403	–6189	–0.26	–3.5
Ca	1.4	41	–3959	–3729	–27	–6.2
LL						
Cu	0.90	0.023	87.31	85.0	0.95	–2.7
Cd	0.75	0.43	31.63	34.7	0.46	8.9
Mn	4.18	2.96	121.9	132	0.31	7.4
Ni	1.50	0.72	76.84	83.5	0.56	8.0
Zn	32.9	19.8	1308.2	139	0.42	6.2
SO_4^{2-}	22.4	25.5	–304.0	–277	–0.12	–9.9
Na	687	682	528	586	0.01	9.9
Ca	209	213	–409.6	–465	–0.02	11.9

^a Fraction retained based on the measured metal mass retained.

^b Percentage difference between calculated mass retained and measured mass retained (negative values indicate a loss).

values reported by Kolstad et al. (2004) for multiple ionic species solutions (Li, Na, Ca, Mg) that ranged from 8.5×10^{-8} to 4.8×10^{-11} m/s for solutions with different ionic strengths at near neutral pH values. The k over time for the LL permeated GCL followed a similar path to the TARD (final k for LL = 4.4×10^{-11} m/s), while the k from the GMW test showed the smallest increase to 2.5×10^{-11} m/s. The comparatively larger increase in k for the ARD samples has been previously observed (Lange et al., 2007; Kashir and Yanful, 2001) and explained by the active replacement of Na by H^+ , divalent and trivalent metals that cause contraction, and possible loss of components due to dissolution, such as calcite—all acting to increase the conductive pore space. For the other solutions, the order of increasing conductivity (GM > TARD > LL) parallels a few distinct factors such as decreasing pH and increasing Ca content. When Ca is present in significant amounts, it can have an adverse effect on Na-bentonites (e.g. Shackelford et al., 2000), causing decreased swell and an increase in hydraulic conductivity (due to contraction of the double layers, see Eglloffstein, 2001). In the TARD, further removal of Cd from solution by lime addition would increase dissolved Ca concentrations. As mentioned, there is a particular concern with the containment of Cd, as it requires a high pH for hydroxide precipitate removal in solution and has shown to be problematic in other systems. Feng et al. (2000) showed that in order to decrease Cd to 2 ppm, the Ca concentration would increase to 400 mg/L. In addition to a cost increase, the increase in Ca could have an eventual adverse impact on the GCL hydraulic conductivity. This research demonstrated that the GCL is able to attenuate Cd to an acceptable level (less than 5 ppm after 10 PV of permeation) at the current pH level of treatment, and maintain a correspondingly low k value.

The pH of the TARD effluent water remained above 6 for the duration of the test. Similarly, the pH of the ARD and LL remained above 6 for about 6 PV of permeation and finally declined to 4.2 and 5.2 after 16 PV of permeation. The considerable buffering capacity of the GCL bentonite has been noted in other studies (e.g. Shan and Lai, 2002).

Significant attenuation of metals from the TARD by the GCL, and the low permeability maintained by the GCL after permeation with more than 16 PV of TARD, demonstrate that GCLs have the potential to serve as an effective barrier material for holding or polishing ponds in which ARD waters that have been treated with lime and still possess some dissolved metal concentration, require a minimum retention time. For example, for a given settlement pond with a hydraulic gradient of 30 [m/m] and k of 3.5×10^{-11} m/s, 16 pore volumes of TARD correlates with a containment time of 4.3 years.

6. Conclusions

Mitigation of ARD is difficult and expensive. Treatment of ARD has become essential to prevent contamination, and, as a result, several methods have been developed (and are continuing to change) to treat ARD, such as the combination of active and passive treatment. This study considered the potential for GCLs to serve as a barrier in holding ponds in which ARD waters that have been treated with lime (termed 'TARD') and still possess some dissolved metal concentration (e.g. Zn, Cd), require a minimum retention time. The behaviour of GCLs in the presence of TARD was measured in terms of metal attenuation capacity and hydraulic conductivity. The results were then compared with other solutions with varying metal and pH contents, including acidic rock drainage (ARD), landfill leachate (LL) and gold mine tailing's porewater (GMW).

Removal efficiencies for metals in the TARD were significantly higher than the average removal efficiencies from the other solutions. Removal efficiencies of greater than 80% in the TARD were

achieved for metals that have been shown to be more difficult to precipitate by lime treatment, such as Ni, Zn, and Cd.

Permeation with 16 PV of TARD resulted in an effluent pH drop from 8.3 to 6.0 (influent TARD pH = 5–5.8); the pH of the ARD effluent waters dropped from 8.3 to 4.2 (influent ARD pH = 2.9).

The permeability of the GCL increased from 1.4×10^{-11} m/s (water) to 3.5×10^{-11} m/s after 16 pore volumes of permeation with the TARD. Permeation with ARD water resulted in an increase in k , from 1.4×10^{-11} m/s to 7.5×10^{-11} m/s. For comparison, a landfill leachate, which is typical of those contained by GCLs in landfills, produced a k value of 4.4×10^{-11} m/s under otherwise similar conditions.

The results of this study suggest that GCLs may be suitable for short-term containment (<4 years) in an active–passive treatment system for ARD. They may be suitable for even longer-term use, but more research would be required to verify this hypothesis. The study demonstrated that the GCL was able to significantly attenuate the low concentration of metals from the TARD solution, and still provide for a low hydraulic conductivity, even in the presence of the elevated Ca from lime treatment.

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References

- Banks, D., Younger, P.L., Arneson, R.T., Iversen, E.R., Banks, S.B., 1997. Mine-water chemistry: the good, the bad and the ugly. *Environmental Geology* 32 (3), 157–174.
- Barton, C.D., Karathanasis, A.D., 1999. Renovation of a failed constructed wetland treating high metal load acid mine drainage. *Environmental Geology* 39, 39–50.
- Bouazza, A., Vangpaisal, T., Abuel-Naga, H., Kodikara, J., 2008. Analytical modelling of gas leakage rate through a geosynthetic clay liner–geomembrane composite liner due to a circular defect in the geomembrane. *Geotextiles and Geomembranes* 26 (2), 122–129.
- Brachman, R.W.L., Gudina, S., 2008. Geomembrane strains from coarse gravel and wrinkles in a GM/GCL composite liner. *Geotextiles and Geomembranes* 26 (6), 488–497.
- Champagne, P., Van Geel, P., Parker, W., 2005. A bench-scale assessment of a combined passive system to reduce concentrations of metals and sulphate in acid mine drainage. *Mine and the Environment* 24, 124–133.
- Chen, F.M., Li, Y.X., 2007. Technology of acid mine drainage treatment by sulphate-reducing bacteria and consideration thereof. *Industrial Water & Wastewater* 38 (1), 17–23.
- Chen, M., Ma, L.Q., 2001. Comparison of three aqua regia digestion methods for twenty Florida soils. *Soil Science Society of America Journal* 65 (2), 491–499.
- Eglloffstein, T.A., 2001. Natural bentonites — influence of the ion exchange and partial desiccation on permeability and self-healing capacity of bentonites used in GCLs. *Geotextiles and Geomembranes* 19 (7), 427–444.
- Environment Canada, 2004. Threats to water availability in Canada. National Water Research Institute, Burlington, Ontario. NWRI Scientific Assessment Report Series No.3 and ACSD Science Assessment Series No.1, 128 pp.
- Feng, D., Aldrich, C., Ta, H., 2000. Treatment of acid mine water by use of heavy metal precipitation and ion exchange. *Minerals Engineering* 13 (6), 623–642.
- Fernandez, F., 1989. The effects of waste leachates on the hydraulic conductivity of natural clays. PhD thesis, The University of Western Ontario.
- Guyonnet, D., Touze-Foltz, N., Norotte, V., Pothier, C., Didier, G., Gailhanou, H., Blanc, P., Warmont, F., 2009. Performance-based indicators for controlling geosynthetic clay liners in landfill applications. *Geotextiles and Geomembranes* 27 (5), 321–331.
- House, W.A., 1998. Interactions of non-volatile micro-organic pollutants. In: Parker, A., Rae, J.E. (Eds.), *Environmental Interactions of Clays*. Springer-Verlag, Berlin, Heidelberg, New York, pp. 55–86.
- Jackson, T.A., 1998. The biogeochemical and ecological significance of interactions between colloidal minerals and trace elements. In: Parker, A., Rae, J.E. (Eds.), *Environmental Interactions of Clays*. Springer-Verlag, Berlin, Heidelberg, New York, pp. 93–180.
- Johnson, D.B., Hallberg, K.B., 2002. Pitfalls of passive mine water treatment. *Reviews in Environmental Science and Biotechnology* 1, 335–343.

- Kalin, M., 2004. Passive mine water treatment: the correct approach? *Ecological Engineering* 22 (4-5), 299–304.
- Kashir, M., Yanful, E.K., 2001. Hydraulic conductivity of bentonite permeated with acid mine drainage. *Canadian Geotechnical Journal* 38 (5), 1034–1048.
- Kolstad, D.C., Benson, C.H., Edil, T.B., 2004. Hydraulic conductivity and swell of nonprehydrated geosynthetic clay liners permeated with multispecies inorganic solutions. *Geotechnical and Geoenvironmental Engineering* 130 (12), 1236–1249.
- Lange, K., Rowe, R.K., Jamieson, H., 2007. Metal retention in geosynthetic clay liners following permeation by different mining solutions. *Geosynthetics International* 14 (3), 178–187.
- Lange, K., Rowe, R.K., Jamieson, H., 2009. Diffusion of metals in GCLs. *Geosynthetics International* 16 (1), 11–27.
- Lange, K., Rowe, R.K., Jamieson, H., Characterization of geosynthetic clay liners using micro-analytical methods: implications for metal mitigation. *Applied Geochemistry*, in press.
- National Orphaned/Abandoned Mines Initiative (NOAMI). Website: <http://www.abandoned-mines.org>, Natural Resources Canada
- Norman, D.K., Raforth, R.L., 1998. Innovations and trends in reclamation of metal-mine tailings in Washington. *Washington Geology* 26(2/3), 29–42.
- Parkhurst, D.L., Appelo, C.A.J., 1999. Users guide to PHREEQC, version 2. PHREEQC Interactive, US Geological Survey.
- Petrov, R.J., Rowe, R.K., Quigley, R.M., 1997. Comparison of laboratory measured GCL hydraulic conductivity based on three permeameter types. *Geotechnical Testing Journal* 20, 49–62.
- Shackelford, C.D., Benson, C.H., Katsumi, T., Edil, T.B., Lin, L., 2000. Evaluating the hydraulic conductivity of GCLs permeated with non-standard liquids. *Geotextiles and Geomembranes* 18 (2-4), 133–161.
- Shan, H.Y., Lai, Y.J., 2002. Effect of hydrating liquid on the hydraulic properties of geosynthetic clay liners. *Geotextiles and Geomembranes* 20 (1), 19–38.
- Sheoran, A.S., Sheoran, V., 2006. Heavy metal removal mechanism of acid mine drainage in wetlands: a critical review. *Minerals Engineering* 19 (2), 105–116.
- Sibrell, P.L., Chambers, M.A., Deaguero, A.L., et al., 2007. An innovative carbonate coprecipitation process for the removal of zinc and manganese from mining impacted waters. *Environmental Engineering Science* 24, 881–895.
- Urase, T., Salequzzaman, M., Kobayashi, S., Matsuo, T., Yamamoto, K., Suzuki, N., 1997. Effect of high concentration of organic and inorganic matters in landfill leachate on the treatment of heavy metals in very low concentration level. *Water Science and Technology* 36 (12), 349–356.
- Younger, P.L., Banwart, S.A., Hedin, R.S., 2002. *Mine Water: Hydrology, Pollution, Remediation*, first ed. Springer, 464 pp.
- Zinck, J.M., Aube, B.C., 2000. Optimization of lime treatment processes. *CIM Bulletin* 93 (1043), 98–105.