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METAL MIGRATION IN GEOSYNTHETIC CLAY LINERS

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ABSTRACT

Geosynthetic clay liners (GCLs) are increasingly being used as low permeability liners to control subsurface contamination by leachate. One concern that is often raised relates to the potential for migration of metals by advection and/or diffusion processes and questions arise regarding the potential attenuation that can occur in a GCL. The research outlined herein studied the migration of select metals (Al, Fe, Mn, Ni, Pb, Cd, Cu, Zn) through GCLs. The objective was to evaluate the potential of GCLs for attenuating the metals present in landfill and mining leachates, and to provide a greater understanding of the factors controlling the performance of a GCL system under these scenarios. Hydraulic conductivity and diffusion tests were conducted on a GCL using different synthetic leachates (municipal solid waste and acid mine drainage solutions with varying metal concentrations). Metal migration was studied through analysis of breakthrough data, and geochemical analysis of effluent waters. Results demonstrating GCL metal attenuation are presented under varying conditions and possible retarding mechanisms are discussed.

RÉSUMÉ

Les recouvrements de membrane argile-géosynthétique (MAG) sont de plus en plus utilisés en tant que recouvrements bas imperméables des remblais pour contrôler la contamination sous la surface souterraine par le lixiviat. Une inquiétude qui est souvent soulevée a trait à la migration potentielle des métaux dans le lixiviat qui, étant déjà de concentration basse, occasionnent des inquiétudes environmentales. La transmission de ces métaux par le MAG peut se faire par des processus d'advection et/ou de diffusion mais peut être atténuée par l'argile de bentonite. La recherche décrite sous pli consiste d'une études de la migration de métaux choisis (Al, Fe, Mn, Ni, Pb, Cd, Cu, Zn) afférant au MAG. L'objectif visé était d'évaluer le potentiel qu'avaient les membranes argile-géosynthétique (MAG) pour atténuer les métaux présents dans les remblais et les lixiviats miniers, et de procurer une meilleure compréhension des facteurs afférant au contrôle de la performance du système MAG en vertu des conditions étudiées. Des essais hydrauliques de conductivité et de diffusion ont été effectués sur un MAG en utilisant différents lixiviats synthétiques (les déchets municipaux solides et les solutions pour le drainages acidiques des mines en tenant compte de concentrations variables du contenu métallique). L'étude de la migration des métaux a été effectuée par l'analyse des données et par l'analyse géochimique des eaux effluentes. Les résultats de l'atténuation du métal sur une membrane argile-géosynthétique (MAG) sont présentés dans le cadre de conditions variables et la possibilité de retards mécaniques est aussi discutée.

1. INTRODUCTION

Geosynthetic Clay Liners (GCLs) have become a well-known substitute to compacted clay liners in landfills and other waste containment facilities. GCLs typically consist of a thin layer of bentonite supported by one or two layers of geosynthetics. The high swelling capacity of the bentonite clay produces a very low saturated hydraulic conductivity that helps prevent subsurface contamination by leachates (Rowe et al., 2004). A recurring issue is the migration of potentially hazardous metals. Because of their strong complexing capacity, metals may be extracted by the high concentration of organic and inorganic ligands present in municipal solid waste leachate, and move easily to the subsurface (Jensen et al., 1999). Comprehensive research has demonstrated that clays have the ability to retain various contaminants, including metals (e.g. Rowe et al., 2004; Abollino et al., 2003; Yong, 2001; Li and Li, 2001). Quigley et al. (1987), observed very slow migration of metals in natural clay from a landfill site, in comparison to other contaminants such as chloride and sodium. However the interaction of metals and GCLs has received very little attention in the literature. These metals can migrate through the GCL by advection and/or diffusion processes and can be attenuated by the bentonite clay. The pH, surface area, and cation exchange capacity of sodium-bentonite used in many GCLs are considerably higher than that of the soils commonly used in a compacted clay liner. The resulting large attenuation capacity of GCLs suggests that they may also be useful in the mining and metal refining industries where metal-rich leachates are a serious problem.

To assess the potential for metal attenuation, this study examined metal (Al, Fe, Mn, Ni, Pb, Cd, Cu, Zn) migration through GCLs in the presence of a municipal solid waste leachate and an acid mine drainage solution. The acid mine drainage solution was designed to evaluate metal retention under more acidic conditions with a lower organic content present than in typical landfill effluents. Metal transport was investigated through continuous flow permeameter and diffusion testing. These tests also enabled the quantification of hydraulic conductivity and buffering capacity of GCLs exposed to various metal-bearing solutions. GCLs were found to be capable of retarding metals, however at specific pH conditions. Both continuous flow and diffusion tests consistently showed delayed breakthrough times for all metals.

2. BACKGROUND AND PREVIOUS WORK

2.1 Interaction and Partitioning of Metals with GCL Na-Bentonite

Bentonite is a naturally occurring material derived from the alteration of volcanic ash, consisting predominantly of the smectite clay mineral montmorillonite (Yong, 2001). Montmorillonite is a three-layer, expanding clay with a large surface area and high cation-exchange capacity. The mineral montmorillonite has a 2:1 configuration consisting of two silicon-oxygen tetrahedral sheets and one aluminum-oxygen-hydroxyl octahedral sheet. In the tetrahedral sheet, the tetravalent silicon (Si^{4+}) is sometimes replaced by trivalent aluminum (Al^{3+}). In the octahedral sheet, the Al^{3+} is replaced by magnesium (Mg^{2+}), iron (Fe^{2+}), zinc (Zn^{2+}) and other cations. Due to these isomorphous substitutions, montmorillonite has a permanent negative charge that attracts interlayer cations that exist in various degrees of hydration thus causing expansion and collapse of the structure. This charge imbalance between the layers is compensated by exchangeable cations (typically, Na^+ or Ca^{2+}). Thicker hydrated shells form around the clay particles in Na-bentonites (in comparison to Ca-bentonites). Na-bentonites also have a smaller crystal size and a finer dispersed micro-structure (Egloffstein, 2001), and thus have a lower hydraulic conductivity.

The chemical interaction between metals and clay soils such as bentonite control the fate of pollutants in many waste containment facilities and thus has been the focus of extensive research (e.g. Papini, 2002). Clays are typically responsible for the immobilization of metals, through mechanisms such as adsorption and precipitation. The extent of immobilization is complex and is related to both the properties of the clay (e.g. CEC, hydrating conditions) and the properties of the aqueous solution such as pH and dissolved ions. The principal mechanisms affecting metal mobility in Na-bentonites have been identified as (i) cation exchange within the clay lattice structure; (ii) cation attraction to broken bonds present at the edges of the clay mineral ($Si\text{-}O^-$ and $Al\text{-}O^-$ groups at the clay particle edges); (iii) precipitation and/or complexation reactions (Yong, 2001). Changes in soil conditions such as pH, redox, or soil solution composition can have a significant impact on metal mobility and are discussed briefly below.

The pH can affect all three mechanisms mentioned either directly or indirectly. Considering mechanism (ii), at pH>8, deprotonation of the hydroxyl groups exposed at the edge surface causes an overall negative charge to be compensated for by cations. At pH values between 2 and 6, most silanol and aluminol groups are protonated, and metal mobility is increased.

For most cationic metals, adsorption increases with pH (Yong, 2001; Abollino et al., 2003). As well, most metal hydroxide, oxide, carbonate, and phosphate precipitates form under alkaline conditions (Lindsay, 1979). At pHs (~4), the dissolution of hydrous oxides like Fe and Mn occur, releasing metal ions to solution.

Since most metals under consideration have more than one oxidation state, changes in redox conditions cause oxidation-reduction reactions to occur and can change the fate of metals in the soil. Fe (III) precipitates as a highly adsorptive ferric oxyhydroxide, whereas under oxygen-deficient reduced conditions, sulfur will tend to form solid sulfides with Fe (II) and other metals.

Several studies have investigated the interaction between metals and bentonite clays. For example, Lo (1992) studied the migration of Pb through a GCL and reported a diffusion coefficient of 5.9×10^{-10} m^2/s and a linear sorption coefficient K_d, of 6000 ml/g. Abollino et al. (2003) studied the sorption of several metals on Na-montmorillonite at different pH values and in the presence of ligands. They found that the pH variations had a significant influence on the mobility of Cu, Pb and Cd. They also found that complex formation (with the organics) hindered the sorption of metals on the clay.

For low hydraulic conductivity materials, i.e. clay, transport is typically governed by diffusion (Rowe et al.. 2004). The diffusion coefficient of a clay material can readily be found using a simple test (Rowe et al., 2004). The current study used an apparatus developed by Lake (2000) to observe metal diffusion in a GCL.

2.1.1 Hydraulic Conductivity

Hydraulic conductivity is the most common performance criterion used in relation to mineral based liners. Hydrating conditions, applied effective stress during permeation, method of manufacture, void ratio and the mass and type of bentonite are all important factors that can affect the hydraulic conductivity of a GCL (Petrov et al., 1997a). In recent years, the chemical compatibility of GCLs with effluents other than water has been examined. For example, a solution high in calcium can actually increase the bulk void ratio and increase the hydraulic conductivity of the GCL. Permeability tests conducted by Egloffstein (2001) using high calcium chloride solutions, resulted in an increase of the permeability of GCLs by approximately a factor of 3-6 compared to the permeability of the original sodium bentonite. Previous studies have consistently shown that a change in the diffuse double layer of cations surrounding the negatively charged clay particles will impact the hydraulic conductivity (Petrov et al., 1997a; Ruhl and Daniel, 1997, Egloffstein, 2001, Yong, 2001). An increase in the diffuse double layer reduces the hydraulic conductivity and shrinkage of the layer will tend to increase hydraulic conductivity.

Although testing in flexible-wall permeameters for measurement of GCL hydraulic conductivity is recommended (Koerner, 1994), other types of permeameters such as the fixed ring permeameter (designed by Fernandez, 1989) are often used for economical purposes and allow equilibrium to be reached within reasonable test times (Petrov et al., 1997b). Using the fixed ring apparatus, Petrov et al. (1997a), found hydraulic conductivity values for GCLs hydrated and permeated with distilled water to range from 5.2×10^{-11} m/s at low confining stresses and 7.5×10^{-12} m/s at higher confining stresses. These tests typically used water as the hydrating fluid and then permeated the sample with the designated liquid to observe changes from a base line value.

Few hydraulic conductivity tests have examined the impact of metal-bearing permeants on GCLs. Although Petrov et al. (1997a) used some trace metals in their influent leachate, the metals were not analyzed at the effluent port. Kashir and Yanful (2001) conducted laboratory experiments that examined the influence of AMD on the hydraulic conductivity of a sodium bentonite paste using a fixed wall permeameter. They measured an average hydraulic conductivity of 2 x 10^{-11} m/s for water and 1 x 10^{-10} m/s for AMD (confining stresses of 30-50 kPa).

3. EXPERIMENTAL PROGRAM

The experimental program consisted of diffusion and hydraulic conductivity testing of the GCLs using different synthetic solutions. The GCL tested in this study was a BENTOFIX™ NW GCL distributed by Terrafix Geosynthetics Inc. The GCL 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 (often denoted as NWL). Rowe et al. (2000) analyzed the properties of the granular bentonite for the NWL GCL. The bentonite mineralogy was found to consist of 91 percent smectite, 5 percent quartz, 3 percent feldspar and 1 percent carbonate. The pore water was analyzed for Cl^- (24 mg/L), SO_4^{2-} (455 mg/L), pH (7.8), Na^+ (12.13 meq/L), Ca^{2+} (1.16 meq/L), Mg^{2+} (0.48 meq/L) and K^+ (0.20 meq/L). The total cation exchange capacity was 91 meq/100g. The average reference mass per unit area bentonite ranged from 4700-5700 g/m^2.

3.1 Sample Preparation

The procedure used to prepare the GCL specimens for hydraulic conductivity and diffusion testing was similar to that described by Petrov et al. (1997a). A steel cutting shoe of the same inside diameter of the diffusion cell (70 mm) or fixed ring cell (54 mm) was placed on the cover geotextile of the GCL, and slowly forced through the GCL specimen using a hydraulic jack assembly with a maximum force of 20 kN. The reference mass per unit area of the bentonite was calculated and the sample was placed immediately from the cutting shoe to the cell for testing. The average reference mass for the current study measured 4720 g/m^2, and the average initial moisture content of the air dried bentonite was 8.5 percent.

3.2 Simulated Leachates

Table 1. summarizes the chemical composition of four synthetic leachate solutions that were used for testing. Three synthetic solutions simulated municipal solid waste (MSW) leachate (modified from Petrov et al., 1997a and Jensen et al., 1999), and one synthetic solution simulated Acid Mine Drainage (AMD) (modified from Champagne, 2001). The synthetic MSW solutions contained a high content of cations typical of that found in MSW (Ca^{2+}, NH^{4+}, Mg^{2+}, K^+), organic acids, anions such as chloride and different metal concentrations of Cu, Mn, Zn, Ni and Pb. To examine the effect of metals present at differing concentrations, three categories were created: MSW with low metal concentration (MLM); MSW with medium metal concentration (MMM); and MSW with high metal concentration (MHM). The MLM permeant was used for the hydraulic conductivity tests and contained equimolar concentrations of Mn, Zn and Ni. The pH was buffered to 5 using NaOH, and the Eh was reduced to -120 mV using a sulfide reducer. The AMD contained a high sulphate concentration, Na, K, a relatively high concentration of metals, and a pH of 3.9. All solutions were prepared by dissolving analytical grade solid crystals into deaired deionized water (DDW). Metal determinations were performed with a Varian Inductively Coupled Plasma Atomic Spectrometer (ICP-AES).

Table 1. Composition of Synthetic MSW and AMD Solutions (units in mg/L)

Component	MLM	MMM	MHM	AMD
Acetic Acid	6200	6200	6200	
Propionic Acid	3610	3610	6310	
Butyric Acid	435	435	435	
Na^+	3670	2000	2000	460
K^+	290	286	286	780
NH_4^+	505	505	500	
Ca^{2+}	714	602	730	
Mg^{2+}	367	365	365	
Cl^-	2250	1200	1200	43
HCO_3^-	3870	3800	3800	
NO_3^{2-}	36	35	35	
SO_4^{2-}	206	200	200	3540
HPO_4^{2-}	15	15	15	
CO_3^{2-}	127	127	127	
$CO(NH_2)_2$	631	635	635	
Al^{3+}				90
Cd^{2+}				6
Cu^{2+}		24	40	20
Fe^{2+}				200
Mn^{2+}	13			25
Zn^{2+}	15	26	45	100
Ni^{2+}	13.4	17	21	20
Pb^{2+}		5.6	9.0	
pH	5.0	5.1	5.1	3.9

3.3 Hydraulic Conductivity Testing

The hydraulic conductivity tests were conducted in the fixed ring permeameter designed by Fernandez (1989), previously used to obtain hydraulic conductivity values for GCLs under confining stresses and permeant solutions similar to the ones in this paper (Petrov et al. 1997a,b).

The fixed ring permeameter consisted of a stainless steel cell where the GCL was encapsulated between an upper and lower porous stone (diameter of 54 mm and a height of 70.5 mm). A static confining stress was applied directly to the top of the specimen by springs sandwiched between locator caps (14 kPa). The GCL was hydrated using DDW under a head of 2-4 cm for a period of time until the measured height did not change. After hydration, the liquid permeant (DDW) was forced through the GCL, while the induced head drop was measured by an in-line pressure transducer, thus allowing for direct calculation of the hydraulic conductivity using Darcy's law. Once the hydraulic conductivity of the DDW remained stable, the permeant was introduced. The effluent (coming out of bottom of cell), was chemically analyzed. Three cells were permeated with MLM and one cell was permeated with AMD.

3.4 Specified Volume Diffusion Testing

A glass apparatus (cylindrical with a 70 mm diameter and ~80 mm height) consisted of a top reservoir separated from a bottom reservoir by a GCL (Lake, 2000). Spacers were adjusted above and below the GCL to ensure swelling to a specified height. A porous disk and filter paper encapsulated the GCL on both sides that ensured even swelling. The GCL was hydrated under a small head (~20 mm). After the GCL was hydrated, (GCL height=10 to 11 mm), DDW was placed above and below the sample. Cl and pH were measured, and once equilibrium was reached, a source solution was placed above the clay sample (source), and the DDW water remained at the bottom (receptor). Samples (0.5 mL) were taken at equivalent time intervals (once a day) from both the source and receptor, and were replaced with water. Five cell tests were completed: 1 MHM; 1 MLM; 2 MMM; 1 AMD.

The contaminant transport through the GCL, was represented by Equation (1). The boundary condition for this test is of the finite mass type (Rowe et al., 2004), and for the source compartment, the concentration at any time, $C_t(t)$, is given by:

$$C_t(t) = C_o - \frac{1}{H_r}\int_0^t f_t(t)dt - \frac{q_c}{H_r}\int_0^t C_t(t)dt \qquad (1)$$

where C_o = initial contaminant concentration [ML^{-3}], at time t[T]; H_r = height of the source fluid [L]; $f_t(t)$ = mass flux of contaminant into the clay at time t [$ML^{-2}T^{-1}$]; q_c = fluid collected for sampling (replaced with DDW) per unit area, per unit time [LT^{-1}]. The receptor concentration at any time, $C_b(t)$, can be expressed as:

$$C_b(t) = C_{bo} - \frac{1}{h_b}\int_0^t f_b(t)dt - \frac{q_c}{h_b}\int_0^t C_b(t)dt \qquad (2)$$

where C_{bo} = initial contaminant concentration in the receptor solution [ML^{-3}]; h_b = height of the receptor reservoir per unit area [L]; $f_b(t)$ = mass flux of contaminant into the receptor at time t [$ML^{-2}T^{-1}$]. The Cl ion for the diffusion tests was modelled by solving Eqs 1-2 using POLLUTE v6 (Rowe and Booker 1997). More detail on solving diffusion coefficients by POLLUTE can be found in Rowe et al. (2000).

4. RESULTS

4.1 Hydraulic Conductivity Testing

The results of a typical hydraulic conductivity test for permeation with the light metal permeant (MLM) are plotted against effluent pore volume (PV) in Figure 1. The hydraulic conductivities for the three cells permeated with MLM correlated well with each other (95% significance). The average hydraulic conductivity during water (DDW) permeation was 3.1×10^{-12} m/s (after 9 PVs). After the introduction of MLM, the hydraulic conductivity increased to a value of 1.6×10^{-11} m/s, followed by a much slower increase. The final value of hydraulic conductivity measured 1.9×10^{-11} m/s after 35 PVs of MLM permeation (total =44 PVs). The pH of the DDW after 9 PVs had passed through the GCL was 8.9 (reference pH). After 11 PVs of the MLM permeant, the pH declined to 8. The pH of the effluent solution reached a minimum of 7.4 at 44 total PVs.

The hydraulic conductivity and pH measurements for permeation with synthetic AMD are shown in Figure 2. At 9 total PVs the hydraulic conductivity of the DDW was 2.8×10^{-12} m/s. Over the next 21 PVs, the hydraulic conductivity showed a steady increase to a value of 1.6×10^{-11} m/s. At 30 PVs, the hydraulic conductivity began to increase at a faster rate (visible by the change in slope in Fig. 2 from 30 PV to 44 PV). The hydraulic conductivity at 44 PVs (after 36 PVs of leachate permeation) was 3.7×10^{-11} m/s. The pH of the DDW (reference pH) permeant was 8.9. The pH remained above 7 (neutral) until 20 PVs. At 21-22 PVs the pH exhibited a drop to 4.6, then dropped again reaching a value of 3.9 at 33 PVs and stayed within the range of 3.8 to 4.9 for the remainder of the experiment.

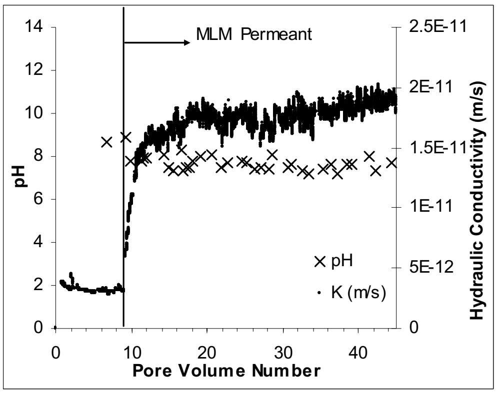

Figure 1. Hydraulic Conductivity with Light Metal Municipal Solid Waste Permeant (MLM) and pH of Effluent Solution versus Effluent Pore Volume Number

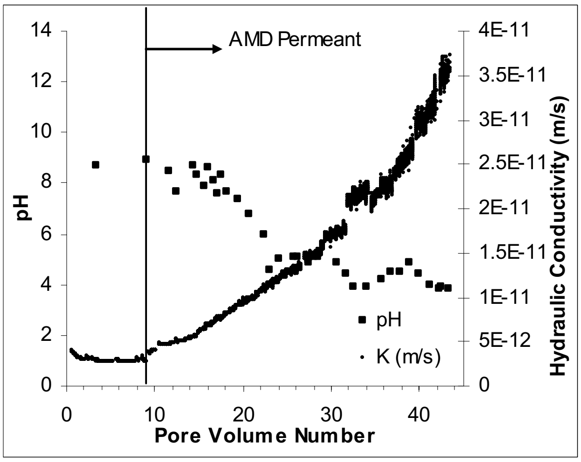

Figure 2. Hydraulic Conductivity with Synthetic Acid Mine Drainage Permeant (AMD) and pH of Effluent Solution versus Pore Volume Number

4.2 Fixed Ring Effluent Concentration Data

Figure 3 shows Cl and metal concentration data measured over time from the effluent sample port of the fixed ring apparatus for the MLM permeant. The effluent Cl concentrations increased and equalled half the influent value (i.e. breakthrough time $C/C_o=0.5$, where C is the effluent concentration, and C_o is the permeant initial concentration) at 11 total PVs (2 PVs of permeant flow). Mn and Ni reached $C/C_o=0.5$ at 12.5 and 13.5 PVs. Zn reached breakthrough at 19.5 PVs and was measured until 26 PVs where it had only reached $C/C_o=0.62$ (Zn measurements beyond this point were in error). In comparison with the Cl ion, the data in Fig. 3 show how the metals were retarded and follow the mobility order (from most to least mobile) of Mn>Ni>Zn. Na effluent values reached $C/C_o=1$ shortly after the permeant was introduced and surpassed that value indicating that Na was being released. The same effect was observed for Ca, though the peak concentration occurred much later.

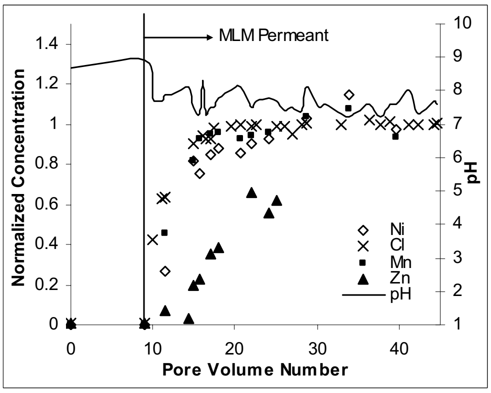

Figure 3. Normalized Metal Concentrations and pH versus Effluent Pore Volume Number for Permeant MLM

Figures 4 and 5 show the effluent concentration data for the cell permeated with AMD. Metals reached their $0.5C_o$ AMD concentrations at the following total PVs: Mn(17.2); Zn(19.5); Ni(21.2); Cd(22.0); Cu(27.0); Fe(27.1); Al(39.2). All metals with the exception of Al eventually reached their influent values. Some metals (Mn, Ni, Cd, Cu and Zn) exhibited effluent concentrations higher than C_o starting at 26 PVs of flow. This prompted examination of pH and other cations (Figure 6). As discussed earlier, the pH exhibited a major drop to 4.6 (22 PVs), then dropped again reaching a value of 3.9 (33 PVs). After the initial drop, Mn and Zn reached a C/C_o value higher than 1. Following the second pH drop, Ni, Cd and Cu reached concentrations higher than influent values. Ca peaked at 22 PVs and decreased steadily after that (Fig. 6). Na had an initial high increase (C/C_o>1) and decreased to a steady value at 22.5 PVs of flow. K and Mg showed a slow and steady increase. It is important to note that the initial Ca and Mg concentrations were both less than 2 mg/L in the permeant solution.

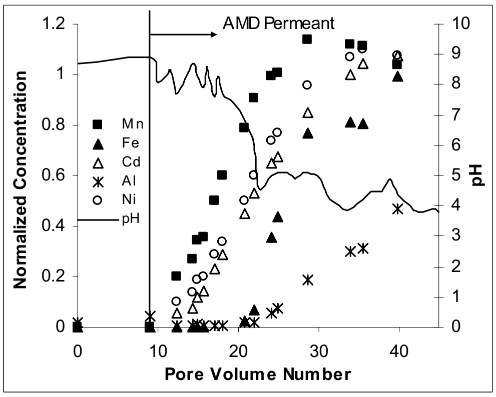

Figure 4. Normalized Metal Concentrations and pH versus Pore Volume Number for Permeant AMD

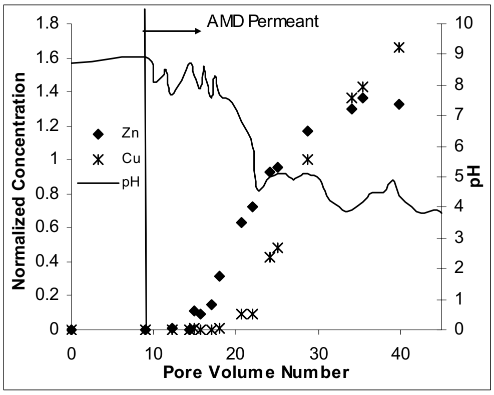

Figure 5. Normalized Metal Concentrations and pH versus Effluent Pore Volume Number for Permeant AMD

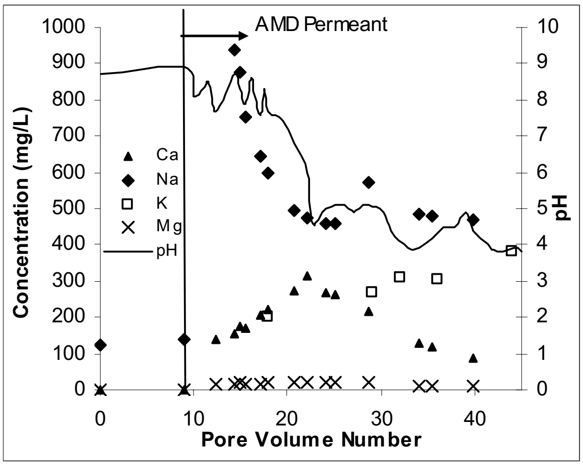

Figure 6. Cation Concentrations and pH versus Effluent Pore Volume Number for Permeant AMD

4.3 Diffusion Testing

Diffusion tests were performed on GCL samples initially hydrated with DDW, followed by the introduction of a source solution (t=0). The average Cl concentration for two cells of MMM solution are shown in Fig. 7. The modelled (POLLUTE) diffusion coefficient of 3.6×10^{-10} m^2/s was best fit to the data (n_t=0.8). Other Cl coefficients were 2.1×10^{-10} m^2/s (MHM) and 3.8×10^{-10} m^2/s (MLM). A typical curve of metal diffusion is shown in Figure 8, with Cu source and receptor values shown over time. The order of mobility was found to be Ni>Zn>Pb>Cu. The AMD Cu behaved similarly (Fig. 9), although the Cu was retained more in the soil. Fig. 10 shows the receptor values for AMD metals. The order of mobility was observed as: Mn>Ni=Cd>Zn>Fe=Cu. Compared to Cl, all metals reached equilibrium at later times.

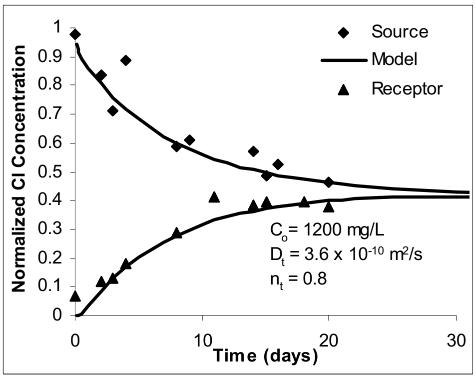

Figure 7. Normalized Chloride Concentrations versus time for medium metal solution (MMM)

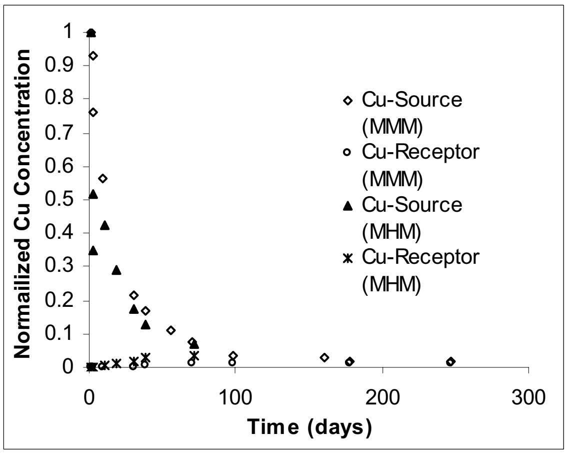

Figure 8. Normalized Cu Concentrations versus time for medium metal and high metal solutions (MMM, MHM)

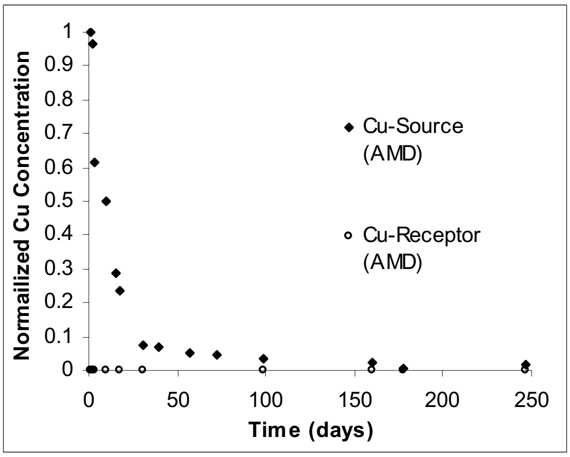

Figure 9. Normalized Cu Concentrations versus time for AMD solution

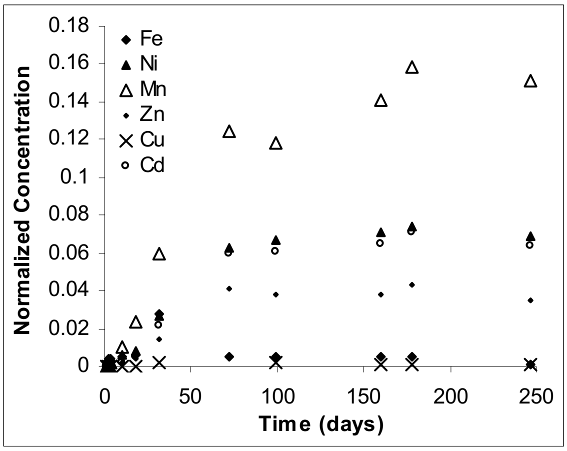

Figure 10. Normalized Metal Concentrations versus time for AMD solution

5. DISCUSSION OF RESULTS

The average hydraulic conductivity during water (DDW) permeation of the GCLs ranged from 2.8x10^{-12} m/s to 3.1x10^{-12} m/s. These values were consistent with those measured by Petrov et al. (1997a) and Ruhl and Daniel (1997). After 35 PVs of leachate permeation, the hydraulic conductivity increased to 1.9x10^{-11} m/s for MLM (factor of 6) and to 3.7x10^{-11} m/s (factor of 13) for AMD. Ruhl and Daniel (1997) permeated GCLs with 0.1 M HCl (pH=1), and found that after 8.5 PVs the hydraulic conductivity increased by a factor of 9, yet the pH did not reach its influent value (due to time restrictions).

The effluent pH of the AMD permeated GCL remained above 7 (neutral) for 11 PVs. After 12 PVs of AMD permeation, the pH dropped to 4.6, then dropped again reaching the influent value of 3.9. Kashir and Yanful (2001) permeated a bentonite paste with an influent AMD solution of pH 3, and found that the pH of the effluent decreased from 7.6 to 3 after only 3 PVs of permeation. The large drop in hydraulic conductivity of the AMD permeated GCL, coincided with the drop in pH. The increase in conductivity was likely due to pore space opening as metals and cations were being mobilized (discussed later) and/or degradation of the clay from the acid (Ruhl and Daniel, 1997). Although the influent pH of the MLM solution was 5.1, after 35 PVs of MLM permeation, the pH only decreased to 7.4. This was likely due to the supply of calcium and carbonate provided by the influent solution in addition to the natural buffering capacity of the GCL.

Effluent data from the fixed ring showed retardation of metals for both the synthetic MSW and AMD leachates. Breakthrough times for Mn and Ni occurred much later for the AMD solution than the MLM solution. This likely occurred since there was much less competition for exchange sites with cationic metals such as Ca in the AMD. Mn and Ni followed very similar curves and in addition to cation exchange, could have been held by Mn oxides. Breakthrough times for Zn were the same for both MLM and AMD, however overall Zn was retained more in the MLM solution. The order of mobility for the MLM metals was Mn>Ni>Zn. Since Zn hydrolyzes at a pH of >7.7 (Yong, 2000), it was likely adsorbed as such a species, and/or exchanged with a cation (e.g. Na). The order of mobility for the AMD leachate was Mn>Zn>Ni>Cd>Cu>Fe>Al. For this case, Zn was more mobile than Ni. This is further indication that Zn was adsorbed as a hydrolyzed form to the clay in the MLM solution. As expected Al was strongly retarded due to the possession of the highest charge (+3). Fe commonly forms oxide precipitates (section 2.1), and was likely adsorbed to the clay structure in such form (other metals may have also been attracted to this surface). Cd may have exchanged with ions as well as precipitated with sulphate. After the first pH drop (4.6), Mn and Zn reached a C/C_o value higher than 1. Following the second pH drop (3.9), Ni, Cd and Cu reached concentrations higher than influent values. This indicates that Mn and Zn could have been adsorbed as hydroxides, or adsorbed to the clays' edges (section 2.1) that were dissociated at the lower pH which resulted in the release of these metals. Although Cu was one of the less mobile metals, it responded strongly to the drop in pH and far exceeded C/C_o=1. Yong (2001) had noted Cu had stronger pH dependence than some metals and showed how Cu precipitates were generally unstable. The curve of Ca and Na also showed how the ions began to decrease at the first drop in pH showing the buffering capacity of the GCL getting lower.

Cl coefficients ranging from 2.1x10^{-10} to 3.8x10^{-10} m^2/s were found for the diffusion tests. These coefficients were on the higher side of similar Cl coefficients measured by Rowe et al. (2000). The order of mobility for both MHM and MMM was found to be Ni>Zn>Pb>Cu. The order of mobility for AMD was observed as: Mn>Ni =Cd>Zn>Fe=Cu. In general, the metals in the AMD solution showed more retention than in the MSW leachates. This is consistent with the fixed ring data.

6. CONCLUSION

The research conducted for this paper subjected GCLs to synthetic MSW leachates and AMD solutions with varying metal concentrations in order to (i) assess the ability of GCLs to attenuate metals and; (ii) examine the properties of GCLs such as hydraulic conductivity and buffering capacity under these scenarios.

GCLs were found to be capable of retarding metals, however at specific pH conditions. Both continuous flow and diffusion tests consistently showed delayed breakthrough times for all metals. Under most conditions, Mn behaved similarly to Cl, indicating that it was the least attenuated metal. Al, Fe and Cu were highly retarded and retained within the clay. Ni, Zn, and Cd were moderately attenuated. Based on arrival times, the metals present in the AMD solution were attenuated more than the metals in the MSW leachate. However a shift in pH caused many metals in the AMD solution to remobilize from the clay back into solution. These observations indicated that the influence of pH and the presence of complexing ligands are important when considering metal mobility.

The effluent pH of the MSW solutions remained in neutral range for up to 35 PVs of leachate permeation. The pH of the AMD effluent remained neutral for 11 pore volumes of permeation, and then decreased to a value of 3.9 after 35 PVs of AMD permeation. The prolonged pH of the MSW effluent was likely the result of the dissolved Ca from the influent in addition to the natural buffering capacity of the GCL. However, Ca could have also been responsible for the lack of metal retention of the MSW solution species compared to the AMD species. Due to the higher retention at higher pHs and the release of metals at lower pHs, adsorption of hydrolyzed species in addition to cation exchange were hypothesized as the mechanisms most responsible for metal retention.

The average hydraulic conductivity of the GCLs permeated with MSW leachate (low metal concentration) increased from 3.1×10^{-12} m/s to 1.9×10^{-11} m/s after 35 PVs of leachate permeation (180 days), and has not reached steady state (currently still in progress). The hydraulic conductivity of the GCLs permeated with AMD increased from 2.8×10^{-12} m/s to 3.7×10^{-11} m/s after 35 PVs of permeation, and is continuing to increase. The drops in hydraulic conductivity for the AMD coincided with decreases in pH and the increase of several metals in effluent solution. The increase in conductivity was likely due to pore space opening as metals and cations were being mobilized and/or degradation of the clay from the acid.

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