Attenuation of Heavy Metals by Geosynthetic Clay Liners

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Abstract

An issue of continuing environmental concern is the migration of potentially hazardous metals in waste containment facilities to the subsurface. Geosynthetic clay liners (GCLs) are now well recognised as an alternative to traditional compacted clay liners. Past research has established the use of clays for attenuating metallic contaminants; however the attenuation capacity of GCLs for metals remains in question. This paper describes research aimed at characterizing GCL behaviour in the presence of metal-rich permeants and assess their potential for metal attenuation in order to evaluate their potential use in different waste containment scenarios. To date, the migration of select metals (Al, Fe, Mn, Ni, Pb, Cd, Cu, Zn) have been investigated using continuous flow permeameters and diffusion testing in the presence of a municipal solid waste leachate and an acid mine drainage solution. The ability of the GCL to attenuate metals was measured by monitoring aqueous solutions before and after the experiment and by bulk analysis of the GCL itself. 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. Delayed breakthrough times and material analysis have shown evidence of metal attenuation and insights into adsorption mechanisms have been made. Material analysis to date has included constituent analysis of digested GCL soil, soil pore water analysis and X-ray diffraction. Future research will use material analysis methods of micro-imaging (electron microprobe, scanning electron microscopy) to further explain retention mechanisms.

Background

Bentonites and other clays have been used to minimize pollutant migration in many waste containment facilities due primarily to their low hydraulic conductivity and ability to immobilize cations. Clays possess the ability to retain metals primarily due to their high specific surface and the negative charges
originating from broken edge bonds and isomorphic substitution of cations in the clay lattice (Yong, 2001; Abollino et al., 2003). Many trace metals are more tightly bound to clay surfaces than the more common soil cations (Lebauve et al., 1988). Geosynthetic Clay Liners (GCLs) consist of a thin layer of bentonite supported by one or two layers of geosynthetics. Although ample research has characterized the behaviour of GCLs with various leachates (e.g. Petrov et al., 1997; Ruhl and Daniel, 1997), the interaction of GCLs with metal-bearing permeants has received little attention. The high quality Na-bentonite in many GCLs contains a high percentage of Na-montmorillonite, which has a large attenuation capacity that implies potential use for immobilizing metals present in landfill leachates and in the mining/metal refining industries. The extent of immobilization is complex and is related to both the properties of the clay (e.g. hyrating conditions) and the properties of the aqueous solution such as pH and presence of other dissolved ions. As a result, a number of studies have focused on metal adsorption to clays, including bentonites, under different environmental conditions (e.g. Li and Li, 2001).

The present research is directed at evaluating the feasibility of employing GCLs for attenuating various metals present in landfill and mining leachates and to providing a greater understanding of the factors controlling the performance of GCL’s. In order to predict the long-term performance of GCLs, it is necessary to examine the mechanism of metal attenuation such as the role of adsorption onto bentonite. The study involves an integrated set of experiments examining the performance of GCLs in hydraulic, diffusion and batch tests using different metal-bearing permeants.

**Materials and Experimental Methods**

Metal migration in GCLs is dominated by advective and diffusive processes with sorption onto the bentonite clay. For this reason, the main experimental program encompasses GCL diffusion (D) and hydraulic conductivity (HC) testing with representative synthetic solutions. Ancillary tests such as batch sorption are also being conducted, however, they are not discussed in this paper. This study uses a BENTOFIX™ NW GCL distributed by Terrafix Geosynthetics Inc. Details of the properties associated with this type of GCL can be found in Rowe et al. (2000). The GCL samples were prepared according to Petrov et al. (1997).

A synthetic municipal solid waste (MSW) leachate with varying metal concentrations and a synthetic Acid Mine Drainage (AMD) solution were created (refer to Table 1 of Lange et al., 2004 for details). The synthetic MSW solutions contain concentrations of organic acid and cations typical of that found in landfill leachate (pH~5). The AMD contained a high sulphate and metal content (pH~3.5). Cationic and metal determinations were performed with an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). A typical ICP analysis determined the concentration of 18 elements (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Zn).
Constant volume diffusion tests were conducted in an apparatus developed by Lake (2000). The apparatus consisted of two reservoirs separated by a GCL. A solution was introduced to the source reservoir, and DDW was placed in the receptor reservoir (zero-gradient across GCL). Quotidian samples were taken from both reservoirs and chemically analyzed (18 element ICP, Cl, pH). Tests were conducted for approximately one year and resulting concentration curves were modelled using POLLUTE v6 (Rowe and Booker 1997). More detail regarding the evaluation of diffusion coefficients is given by Rowe et al. (2000) and Rowe et al. (2004).

Hydraulic conductivity (HC) testing was conducted in the fixed ring permeameter designed by Fernandez (1989). Details regarding sample setup and testing using this instrument is given by Petrov et al. (1997). Briefly, the fixed ring permeameter consists of a stainless steel cell containing the GCL (D= 54 mm; H=70.5 mm). A confining stress (14 kPa) is applied to the top of the specimen by springs. After hydration of the GCL, distilled de-aired water (DDW) is forced through the GCL, while the induced head drop is measured thus allowing for calculation of the HC. After a period of DDW permeation, a leachate is forced through the GCL and the effluent is tested periodically (18 elements ICP, Cl, pH).

Following completion of diffusion and HC testing, GCLs were cut into pie shaped sections and analyzed. Pore water was squeezed from the GCL samples and analyzed by ICP. The elemental composition and adsorbed cations to the clay was found by acid digestion of the clay using the aqua regia method (Chen and Ma, 2001), followed by ICP analysis. X-ray diffraction (Philips X-Pert MPD) was used to identify minerals present in the clay, and precipitates found on the surface of the GCL and in the effluent waters.

**Results and Discussion**

Measured Cl diffusion was similar to Lake’s (2000) results, in that equilibrium was reached at ~ 20 days and diffusion coefficients were within the same range (3.6x10^{-10} m^2/s). Although equilibrium was generally reached after approximately 120 days for most metals, tests were continued for 1 year to estimate long term effects. The graph of Ni^{2+} diffusion (AMD) versus time in Fig. 1 represents a typical metal diffusion curve. Both source and receptor values began to approach equilibrium at ~ 50 days. The Ni^{2+} present in the MSW leachate followed a similar curve, but in general, the metals in the AMD solution showed more retention than in the MSW leachates. The order of mobility for the MSW metals (from most to least mobile) was found to be Ni>Zn>Pb>Cu. The order of mobility for the AMD metals was observed as: Mn>Ni=Cd>Zn>Fe=Cu.
Figure 1. Diffusion curve for nickel (AMD), normalized concentration vs. time.

Figure 2 shows a plot of an HC test for permeation with the MSW leachate as a function of effluent pore volume (PV). The permeant was introduced after 9 PVs of DDW permeation. Although the influent pH of the MSW solution was 5.1, after 44 total PVs, the pH decreased to 7.4 (compared to 8.9 with DDW). This was likely due to the buffering capacity provided by calcium carbonate in the bentonite. The average conductivity (k) of the DDW saturated GCLs measured with respect to DDW was 3.1x10^{-12} m/s. After the introduction of the MSW leachate, k increased to a final value of 1.9x10^{-11} m/s.

Figure 2. Hydraulic conductivity, pH vs. pore volume no. for MSW permeant.

Figure 3 shows the HC and pH measurements for permeation with AMD. The effluent pH of the AMD permeated GCL remained above 7 until 20-22 PVs, where it dropped to 4.6, then dropped again to ~3.8. The hydraulic conductivity, k, increased to 1.6x10^{-11} m/s from the initial DDW k of 2.8x10^{-12}. At 30 PVs, k began to increase at a faster rate (visible by the change in slope in Fig. 3 from 30 PV to 44 PV) to a final k at 44 PVs of 3.7x10^{-11} m/s. The largest increase in k of the AMD permeated GCL coincided with the drop in pH. The increase in k was likely due to pore space opening as metals and cations were being mobilized by the adsorption of H^+ (shown later in fixed ring data) and/or degradation of the clay from the acid (Ruhl and Daniel, 1997).
Figure 3. Hydraulic conductivity, pH vs. no. of pore volumes for AMD.

**Fixed Ring Effluent Concentration Data**

Figure 4 shows data recorded over time from the effluent sample port of the fixed ring apparatus for the MSW permeant. The effluent Cl reached breakthrough (i.e. time when concentration reaches half of its’ initial $C/C_o=0.5$, where $C =$ effluent concentration; $C_o =$ initial concentration) at 11 total PVs. Mn, Ni and Zn reached $C/C_o=0.5$ at 12.5, 13.5, and 19.5 PVs respectively. In comparing with Cl, Fig. 4 shows how the metals were retarded and follow the mobility order of Mn>Ni>Zn.

Figure 5 shows the effluent concentration data for the cell permeated with AMD. Metals reached breakthrough ranging from 17.2 to 39.2 PVs. Breakthrough times for Mn and Ni occurred much later for the AMD solution than the MSW solution. Initially, the AMD GCL was able to adsorb more metals due to less competition for exchange sites than for the metals in the MSW (large quantity of Ca, K). Al did not reach its’ influent value and was likely strongly retarded due to the possession of the highest charge (+3). Fe also experienced strong retention and was precipitated as a hydroxide (evident from the presence of an orange/red layer in the GCL). Some metals (Mn, Ni, Cd, Cu and Zn) exhibited effluent $C/C_o>1$ starting at 26 PVs, coincident with the drop in pH, indicating that metals were being released from the GCL. This also correlates to the increase in $k$ where metals being remobilized may have caused pore space to open up. Mn and Zn could have been adsorbed as hydroxides or adsorbed to the clay edges that were dissociated at the lower pH, resulting in the release of these metals.
Table 3 shows the amount of metals retained onto the soil for the MSW and AMD diffusion cells respectively. The total amount of metals found in the pore water and soil was similar, but consistently less than the estimated amount retained within the soil (difference between source and receptor mass over time). The difference may be in part explained through error in the loss of soil measurement, and analytical technique, however, it is not yet fully explained. This data shows how the diffusion and fixed ring (not shown here) order of retention (from least to most retained) follows the same order as that for mobility (previous section) Ni>Zn>Pb>Cu for the MSW leachate. The AMD order is also identical to that of the AMD diffusion cell and fixed ring order: Mn>Ni>Cd>Zn>Fe=Cu. X-ray diffraction identified precipitates on the GCL from the AMD diffusion cell as calcium manganese oxide and magnesium calcite. The presence of carbonates suggests that carbonate metal precipitates may have been responsible for metal attenuation in both the MSW and AMD systems.
Table 3. Diffusion Cell MSW (330 days)

<table>
<thead>
<tr>
<th>Units= mg</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
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<tbody>
<tr>
<td>Mass lost from source</td>
<td>3.73</td>
<td>2.03</td>
<td>1.02</td>
<td>3.89</td>
</tr>
<tr>
<td>Mass recovered in receptor</td>
<td>0.070</td>
<td>0.45</td>
<td>0.043</td>
<td>0.44</td>
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<td>Mass retained in GCL *</td>
<td>3.66</td>
<td>1.58</td>
<td>0.98</td>
<td>3.45</td>
</tr>
<tr>
<td>Percentage retained in GCL</td>
<td>~98%</td>
<td>~78%</td>
<td>~96%</td>
<td>~89%</td>
</tr>
<tr>
<td>Measured GCL Pore water</td>
<td>0.0053</td>
<td>0.018</td>
<td>0.0010</td>
<td>0.0020</td>
</tr>
<tr>
<td>Measured GCL Bentonite</td>
<td>2.26</td>
<td>1.33</td>
<td>0.95</td>
<td>3.19</td>
</tr>
<tr>
<td>Total Measured **</td>
<td>2.27</td>
<td>1.35</td>
<td>0.95</td>
<td>3.19</td>
</tr>
</tbody>
</table>

* Difference between source and receptor mass over the given time period.
** Total of measured pore water and bentonite

Conclusions

GCLs were found to be capable of significantly retarding metals, with the potential for retardation depending on the mass loading, pH and permeant composition. Delayed breakthrough times through diffusion and HC testing consistently showed metal attenuation and metals found in the GCL by material analysis proved that metal immobilization was occurring. A shift in pH caused many metals in the AMD solution to remobilize from the clay back into solution once the buffering capacity was exhausted. Due to metal retention at high pH and the release at low pHs, adsorption of hydrolyzed species in addition to cation exchange were hypothesized as the mechanisms most responsible for metal retention. The average GCL hydraulic conductivity during water (DDW) permeation ranged from $2.8 \times 10^{-12}$ m/s to $3.1 \times 10^{-12}$ m/s. After 35 PVs of leachate permeation, the hydraulic conductivity increased to $1.9 \times 10^{-11}$ m/s for the MSW leachate and to $3.7 \times 10^{-11}$ m/s for AMD; both still very low values. The increase in hydraulic conductivity for the AMD coincided with decreases in pH and the increase of several metals in effluent solution.

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References
