Diffusion of sodium and chloride through geosynthetic clay liners

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Received 4 February 1999; received in revised form 19 July 1999; accepted 21 August 1999

Abstract

The diffusion coefficients deduced from GCL diffusion tests performed with 3 g/L to 5 g/L (0.05 M to 0.08 M) NaCl solutions decrease linearly with decreasing final bulk GCL void ratio. However, this diffusion coefficient is shown to be dependent on the source solution and, when the NaCl concentration is increased significantly, the diffusion coefficient deduced is also shown to increase. For the range of products examined, it is shown that the method of GCL manufacture did not significantly affect the diffusion coefficients. Different methods of performing the test are examined and it is shown that the type of diffusion test has little effect on the diffusion coefficient deduced at a given void ratio for the range of NaCl concentrations examined (3 g/L to 5 g/L). However, as the NaCl concentration increases to 0.6 M or 2.0 M, a constant stress applied to the sample is shown to mitigate increases in diffusion coefficients compared to the case of the sample being tested at a constant void ratio. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: GCL; Landfill; Diffusion; Contaminant transport; Chloride; Sodium; Leachate

1. Introduction

The advective migration of contaminants through geosynthetic clay liners (GCLs) and GCL composite liner systems has been examined by numerous investigators (see Rowe, 1998 for a review). For typical design situations the advective flow rates through a GCL liner system are very low and chemical (molecular) diffusion may be
the dominant transport mechanism through the GCL liner system. Unfortunately there is a paucity of research relating to diffusion of contaminants through GCLs (see Lo, 1992; Rowe et al., 2000; Lake and Rowe, 2000).

When GCLs are placed as part of municipal solid waste landfill bottom (base) liners, the GCL will be subjected to a variety of different stresses ranging from low stresses before addition of the waste (\(\sim 5-20\) kPa) to very high stresses after the landfill has been filled with waste and capped (\(\sim 100-400\) kPa). The GCL may also be subjected to a variety of hydration conditions such as being hydrated under relatively low stresses by the moisture from underlying soil and being subsequently consolidated by the weight of the overlying waste. Further complicating matters is the fact that the GCL may be subjected to leachates with different concentrations and compositions. The different possible combinations of stress conditions, hydration conditions and permeating fluids will result in a wide range of final bulk GCL void ratios (see Appendix A for a definition) and one may anticipate that this may have an effect on the diffusive behavior of contaminants migrating through the GCLs.

This paper will examine the effect of different stress conditions and corresponding different GCL final bulk void ratios, different contaminant source solutions (NaCl and a synthetic municipal solid waste leachate), two different diffusion test methods, and the type of GCL manufacturing process on GCL diffusion coefficients. Based on these results, factors to consider when assessing diffusion coefficients for GCL liner systems are discussed.

2. Materials tested

The three GCLs examined in this study are summarized in Table 1 together with the generic symbols used to identify the products in the remainder of the paper. They

<table>
<thead>
<tr>
<th>Symbol used in this paper</th>
<th>GCL type</th>
<th>Middle bentonite layer</th>
<th>Carrier geotextile</th>
<th>Cover geotextile</th>
<th>Minimum mass/area tested, (M_{\text{GCL}}) (g/m(^2))</th>
<th>Mean, standard deviation of (M_{\text{GCL}}) (g/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NWNWT</td>
<td>NW</td>
<td>Granular sodium bentonite</td>
<td>PP nonwoven(^b)</td>
<td>PP nonwoven</td>
<td>5270</td>
<td>5898, 312</td>
</tr>
<tr>
<td>WNT</td>
<td>NS</td>
<td>Granular sodium bentonite</td>
<td>PP woven</td>
<td>PP nonwoven</td>
<td>5665</td>
<td>5795, 113</td>
</tr>
<tr>
<td>WNWBT</td>
<td>BFG5000(^c)</td>
<td>Powder sodium bentonite</td>
<td>PP woven</td>
<td>PP nonwoven</td>
<td>5481</td>
<td>5578, 85</td>
</tr>
</tbody>
</table>

\(^a\)Notes: PP: Polypropylene

\(^b\)Scrim reinforced with slit film woven geotextile.

\(^c\)Cover geotextile filled with 500 g/m\(^2\) of powder bentonite.
included Bento-fix NW and NS GCLs (distributed by Terrafix Geosynthetics Inc., based in Rexdale, Ontario, Canada and Naue Fasertechnik in Lubbecke, Germany under slightly different product identifiers, Bento-fix B4000 and NSP 4900-3) and BFG5000 GCLs (distributed by Naue Fasertechnik in Germany). The generic symbols used to describe these GCLs throughout the rest of the paper are such that the type of manufacturing of each GCL can be ascertained from the symbols (see Table 1). The first ‘NW’ or ‘W’ in the generic name refers to whether the bottom geotextile (sometimes called the “carrier” geotextile) is nonwoven or woven. The second ‘NW’ describes the top (“cover”) geotextile which was nonwoven for all GCLs examined herein. The ‘B’ in the generic name WNWBT refers to if bentonite is impregnated in the top geotextile and the ‘T’, if present, refers to the needlepunched fibres being thermally treated.

The sodium bentonite used in these GCLs is predominately smectite (~90%) with initial bentonite pore water chemistry showing Na\(^+\) (0.26 g/L or 0.011 M) and SO\(_4^{2-}\) (0.46 g/L or 0.005 M) to be the predominant ions in the pore fluid when the soil was wetted to its saturation moisture content and squeezed at a pressure of 10 MPa (Rowe et al., 2000).

### 3. Procedures and tests performed

Two types of diffusion tests were performed to examine the influence of contaminant source solution, applied stress and the type of GCL on the diffusion coefficients for sodium and chloride. Specified volume diffusion (SVD) tests allowed comparison of diffusion results by controlling the final bulk GCL void ratios while constant stress diffusion (CSD) tests allowed comparison of diffusion coefficients at similar specified applied stresses. The test procedures and methods of data analysis for both types of diffusion tests have been described in detail by Rowe et al. (2000) and are summarized below for clarity.

The specified volume diffusion (SVD) testing apparatus shown in Fig. 1 consists of a lower ring (receptor reservoir), a middle ring (GCL sample holder) and an upper ring (source reservoir), all made of acrylic. Rigid porous steel plates, the same diameter as the outside edge of the middle ring, are placed above and below the middle ring to prevent the GCL from swelling beyond the thickness of the middle ring. When the diffusion cell is assembled with the threaded rods (see Fig. 1), the GCL is hydrated and begins to swell with the spacer rods placed in the upper and lower reservoirs assisting in constraining the movement of the porous steel plates. By manufacturing different ring heights (5.6 mm, 7.1 mm, 9.1 mm, and 11.0 mm), control over the bulk GCL void ratio can be maintained during testing.

Similar to the SVD apparatus, the constant stress diffusion (CSD) test apparatus shown in Fig. 2 consists of an acrylic lower ring (receptor reservoir) and an acrylic upper ring (source reservoir). However, instead of placing the sample in a middle ring, the sample is supported by a porous steel plate, which rests on a ridge in the lower ring and the lower spacer rod. Unlike the SVD test apparatus, the top porous steel plate is the same diameter as the upper reservoir and is free to move in the upper ring when
the sample hydrates (or contracts due to changes in pore fluid composition). The purpose of the upper spacer rod, which sits on the upper porous steel plate, is to support a plunger that extends through the top of the cell. This plunger supports a load frame that allows application of a stress to the sample during hydration and diffusion testing of the GCL.

Prior to diffusion testing, GCL samples were cut and placed in the diffusion cell as described in Rowe et al. (2000). The GCL samples were hydrated with de-ionized, de-aired water (DDW) from the bottom of the sample and the amount of water uptake was recorded using a burette attached to the bottom reservoir of the GCL diffusion testing apparatus. When water uptake ceased, 1 cm of DDW was added to the source compartment and the sample was left until chemical equilibrium was reached in the source and receptor compartments. A diffusion test was then initiated by replacing the 1 cm of DDW in the upper chamber by the contaminant source solution of interest such that there was no head difference across the GCL. Samples of both the source and receptor (3 ml) were taken daily and replaced with equal volumes of de-ionized,
distilled water. Cation analyses of samples were performed using an atomic absorption spectrometer and anion analyses were performed using ion chromatography.

Two different source solutions were used for diffusion testing: (a) an NaCl solution at a range of concentrations to be discussed, and (b) a synthetic leachate solution similar to the composition of that observed at the Keele Valley Landfill in Toronto, Ontario, Canada. The nominal concentrations of the major constituents of the synthetic leachate are given in Table 2.

The diffusion tests are summarized in Table 3. In the “test number” column, the first part of the test number symbol (e.g. NWNWT, WNWBT) corresponds to the generic GCL symbols used in Table 1. This is followed by a test number (1, 2, ..., 6; A, B, etc.) followed by a designation –SV or –CS which indicates the type of test performed with –SV indicating that it was a specified volume diffusion (SVD) test.
Table 2
Composition of synthetic leachate used for GCL diffusion testing*

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration/value (mg/L unless otherwise noted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>6000</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>4000</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>600</td>
</tr>
<tr>
<td>Na⁺</td>
<td>4705</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>1040</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>405</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>555</td>
</tr>
<tr>
<td>K⁺</td>
<td>320</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>3800</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>125</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>330</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>35</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>4260</td>
</tr>
<tr>
<td>HPO₄³⁻</td>
<td>15</td>
</tr>
<tr>
<td>pH</td>
<td>6 [ -   ]</td>
</tr>
<tr>
<td>Eh</td>
<td>-120 [ mV ]</td>
</tr>
</tbody>
</table>

*Notes: Trace metal solution added to leachate containing Fe²⁺, Zn²⁺, Cu²⁺, Mn²⁺, Al³⁺, Co²⁺. Concentration of Na⁺ varies due to addition of Na₂S₂ reducing agent to obtain desired Eh and NaOH to obtain desired pH.

or –CS indicating a constant stress diffusion test (CSD). In the column “Test type”, the number in parentheses denotes either the height to which the GCL was allowed to swell (SVD) or the stress at which the diffusion test was performed (CSD). All samples were hydrated with de-aired, de-ionized water and diffusion tests were conducted with a 4.6 g/L NaCl source solution unless otherwise noted.

To obtain experimental diffusion coefficients, it is necessary to fit a theoretical curve to the experimental data. All modeling was performed with the latest version of the finite-layer contaminant transport program POLLUTE (Rowe and Booker, 1999). The source and receptor reservoirs were specified as finite mass boundary conditions with provisions to account for the mass of contaminant removed by sampling. The initial concentration profile in the sample was the concentration of the receptor solution at the end of the hydration period. The details of the modeling procedure are given in Rowe et al. (2000).

Figs. 3 and 4 show examples of chloride and sodium concentration profiles plotted in terms of the normalized concentration (i.e. source and receptor values are divided by the initial source concentration, c₀) for test NWNWTA-CS. The data points (solid circles) in each figure represent the experimentally measured concentrations for chloride (Fig. 3) and sodium (Fig. 4). The bottom data and curve in each figure are the observed and calculated concentration increase in the receptor. The net increase in mass of contaminant in the receptor is the difference between the increase in mass due to diffusive flux from the sample minus the decrease in mass due to sampling and
Table 3
GCL Diffusion Tests (all performed with 4.6 g/L NaCl solution unless otherwise noted)*

<table>
<thead>
<tr>
<th>Test number</th>
<th>Test type</th>
<th>Chloride diffusion coefficient, $D_c$ (m²/s)</th>
<th>Sodium diffusion coefficient¹, $D_s$ (m²/s)</th>
<th>Final bulk GCL void ratio, $e_B$ (—)</th>
<th>Bentonite total porosity, $n_t$ (—)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NWNWT1-SV</td>
<td>SVD (7.1 mm)ᵇ</td>
<td>$1.5 \times 10^{-10}$</td>
<td>$2.5 \times 10^{-10}$</td>
<td>2.1</td>
<td>0.73</td>
</tr>
<tr>
<td>NWNWT2-SV</td>
<td>SVD (11.1 mm)ᵇ</td>
<td>$3.0 \times 10^{-10}$</td>
<td>$5.0 \times 10^{-10}$</td>
<td>3.2</td>
<td>0.80</td>
</tr>
<tr>
<td>NWNWT3-SV</td>
<td>SVD (5.6 mm)ᵇ</td>
<td>$3.5 \times 10^{-11}$</td>
<td>$6.0 \times 10^{-11}$</td>
<td>1.1</td>
<td>0.56</td>
</tr>
<tr>
<td>NWNWT4-SV</td>
<td>SVD (9.1 mm)</td>
<td>$2.8 \times 10^{-10}$</td>
<td>$4.4 \times 10^{-10}$</td>
<td>2.7</td>
<td>0.78</td>
</tr>
<tr>
<td>NWNWT5-SV</td>
<td>SVD (7.1 mm)</td>
<td>$1.4 \times 10^{-10}$</td>
<td>$2.2 \times 10^{-10}$</td>
<td>1.7</td>
<td>0.67</td>
</tr>
<tr>
<td>NWNWT6-SV</td>
<td>SVD (7.1 mm)ᶜ</td>
<td>$2.2 \times 10^{-10}$</td>
<td>N/A</td>
<td>1.9</td>
<td>0.70</td>
</tr>
<tr>
<td>WNWT1-SV</td>
<td>SVD (7.1 mm)ᵇ</td>
<td>$1.6 \times 10^{-10}$</td>
<td>$2.7 \times 10^{-10}$</td>
<td>2.0</td>
<td>0.69</td>
</tr>
<tr>
<td>WNWT2-SV</td>
<td>SVD (9.1 mm)</td>
<td>$2.7 \times 10^{-10}$</td>
<td>$4.0 \times 10^{-10}$</td>
<td>2.9</td>
<td>0.77</td>
</tr>
<tr>
<td>WNWT3-SV</td>
<td>SVD (5.6 mm)</td>
<td>$7.2 \times 10^{-11}$</td>
<td>$1.1 \times 10^{-10}$</td>
<td>1.3</td>
<td>0.59</td>
</tr>
<tr>
<td>WNWT1-SV</td>
<td>SVD (7.1 mm)ᵇ</td>
<td>$1.3 \times 10^{-10}$</td>
<td>$2.5 \times 10^{-10}$</td>
<td>2.1</td>
<td>0.74</td>
</tr>
<tr>
<td>WNWT2-SV</td>
<td>SVD (11.1 mm)</td>
<td>$2.9 \times 10^{-10}$</td>
<td>$4.3 \times 10^{-10}$</td>
<td>3.6</td>
<td>0.83</td>
</tr>
<tr>
<td>WNWT3-SV</td>
<td>SVD (9.1 mm)</td>
<td>$2.8 \times 10^{-10}$</td>
<td>$4.4 \times 10^{-10}$</td>
<td>2.8</td>
<td>0.79</td>
</tr>
<tr>
<td>NWNWTA-CS</td>
<td>CSD (22 kPa)</td>
<td>$2.9 \times 10^{-10}$</td>
<td>$4.8 \times 10^{-10}$</td>
<td>2.8</td>
<td>0.78</td>
</tr>
<tr>
<td>NWNWTA-CS</td>
<td>CSD (145 kPa)</td>
<td>$1.3 \times 10^{-10}$</td>
<td>$2.1 \times 10^{-10}$</td>
<td>1.8</td>
<td>0.69</td>
</tr>
<tr>
<td>NWNWTC-CS</td>
<td>CSD (145 kPa)ᶜ</td>
<td>$2.3 \times 10^{-10}$</td>
<td>$4.0 \times 10^{-10}$</td>
<td>2.6</td>
<td>0.77</td>
</tr>
<tr>
<td>NWNWTD-CS</td>
<td>CSD (145 kPa)</td>
<td>See Table 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NWNWTE-CS</td>
<td>CSD (22 kPa)ᶜ</td>
<td>$3.7 \times 10^{-10}$</td>
<td>N/A</td>
<td>2.6</td>
<td>0.77</td>
</tr>
<tr>
<td>NWNWTF-CS</td>
<td>CSD (145 kPa)ᶜ</td>
<td>$2.2 \times 10^{-10}$</td>
<td>N/A</td>
<td>1.8</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.0 \times 10^{-10}$</td>
<td></td>
<td>1.6</td>
<td>0.67</td>
</tr>
</tbody>
</table>

*SVD: Specified volume diffusion test; CSD: Constant stress diffusion test. All samples hydrated with deionized, distilled water.

ᵇSource was 3.3 g/L NaCl.

ᶜSource was synthetic leachate.

ᵈHydrated at 3 kPa and then consolidated to 145 kPa before diffusion test.

⁵Test is not plotted in Fig. 3.

¹Based on $K_d = 0$ ml/g.

ⁿDiffusion coefficients for sample thickness at beginning and end of diffusion test (see text).

replacement of the extracted fluid with distilled water (which is considered in the modelling). Referring to Fig. 4, it is noted that after approximately ten days, both the observed and calculated concentration of sodium in the receptor begins to decrease slightly due to dilution from sampling and replacement of fluid. The different initial concentrations of sodium and chloride in the receptor (Figs. 3 and 4) give rise to different shapes of chloride and sodium receptor curves due to different amounts of mass being removed during the sampling process. The top data and curve shows the observed and calculated decreases in concentration in the source solution due to diffusive flux into the GCL and sampling. A good fit to both the source and receptor experimental data were obtained using the parameters given in Figs. 3 and 4.

As discussed by Rowe et al. (2000) batch tests performed with NaCl solutions and granular bentonite in these tests found an upper bound value of $K_d$ of 0.12 ml/g for
sodium. Fig. 4 includes the theoretical curves for both $K_d$ of 0 ml/g and $K_d$ of 0.12 ml/g ($D_t = 4.8 \times 10^{-10}$ m$^2$/s for both). The curves are usually indistinguishable for these two $K_d$ values which suggests that sorption does not have a significant effect on deduced Na$^+$ and Cl$^-$ diffusion coefficients and corresponding fluxes for the cases considered. Rowe et al. (2000) noted that some osmotic flow is observed in diffusion tests such as this but also showed that this osmosis had no significant effect on the diffusion of sodium chloride for these tests. Rowe et al. (2000) also discussed the process of anion exclusion and how it could affect GCL diffusion test results.
The tests summarized in Table 3 utilized finite mass boundary conditions for the source and receptor which essentially means that the mass of contaminant in the source (or receptor) at any time, \( t \), is equal to the initial mass in the source (or receptor) minus the mass flux into the sample (plus mass flux out of the sample for receptor) minus the mass lost due to sampling. With no advective transport though the sample, this flux, \( f \), at any point in the GCL can be expressed in terms of the porous media diffusion coefficient \( D_p = n_e D_e \),

\[
f = -n_e D_e \frac{dc}{dz} = -D_p \frac{dc}{dz}
\]

In principle, the diffusion through a porous media is a function of both the effective porosity, \( n_e \), and the effective diffusion coefficient, \( D_e \). However, it was found that except at very small times (of no practical consequence), the precise values of the effective porosity, \( n_e \), and effective diffusion coefficient, \( D_e \), are not critical to predicting transport through a single GCL provided the range of values of \( n_e \) and \( D_e \) correspond to the same total product \( D_p = n_e D_e \). There was very little latitude in the selection of a value of \( D_p \) that would fit the experimental data (Rowe et al., 2000). This approach of using \( D_p \) is convenient since generally only the total porosity, \( n_t \), is known for a GCL and the effective porosity, \( n_e \), may vary from one contaminant to another or with other factors such as the void ratio. Therefore, the diffusion coefficients reported in this paper, \( D_t \), are the values deduced from the experimental data for \( n = n_t \) (i.e. \( D_p = n_t D_t \)) and are not effective diffusion coefficients, \( D_e \).

To demonstrate that the combination of \( n \) and \( D \) giving rise to \( D_p \) is not critical for a relatively thin sample such as a GCL, two samples of different lengths (sample \( A = 10 \text{ mm} \) (GCL), sample \( B = 100 \text{ mm} \) with the same total porosity \( n_t = 0.7 \) and the same diffusion coefficient \( (D_t = 1.5 \times 10^{-10} \text{ m}^2/\text{s}) \) are considered. The solid lines on Fig. 5 show the theoretical concentration profiles generated with POLLUTE (Rowe and Booker, 1999) through both the thin and relatively thick sample at the end of 20 days. If the effective porosity, \( n_e \), was known for the sample (for example, \( n_e = 0.3 \) and the effective diffusion coefficient, \( D_e \), was \( 3.5 \times 10^{-10} \text{ m}^2/\text{s} \) (i.e., yielding the same value of \( D_p = 1.05 \times 10^{-10} \text{ m}^2/\text{s} \) as for the solid line), the profile through the thin sample (shown by the long dashed line) is practically identical to the solid line for the thin sample but quite different for the thicker sample B. To illustrate that the choice of \( D_p \) is important even for a thin sample, the calculated profile is also shown at 20 days for \( n_e = 0.3 \) and \( D_e = 1.5 \times 10^{-10} \text{ m}^2/\text{s} \) \( (D_p = 0.45 \times 10^{-10} \text{ m}^2/\text{s}) \). It can be seen that this gives a much different curve than that obtained for \( D_p = 1.05 \times 10^{-10} \text{ m}^2/\text{s} \) for both the thin and thick sample. Thus for a GCL it is important to establish \( D_p \), but the combination of \( n \) and \( D \) that give rise to this value of \( D_p \) is not critical for practical applications and the range of parameters as indicated by Rowe et al. (2000).

However it should be noted that while the porous media diffusion coefficient approach is suitable for a single GCL, it may not be suitable if multiple layers of GCL are used and the layer ceases to be thin (~ 1 cm or less). More investigation would be required if one was considering the use of multiple layers of GCL, however since this is not usually the case in practice, it is not discussed further here.
3.1. Effect of final bulk GCL void ratio on diffusion coefficient

The final bulk GCL void ratio, defined by Petrov et al. (1997) as the ratio of the volume voids to the volume of solids in the GCL (geotextiles included) at the end of testing (see Appendix A), provides a good basis for evaluating data obtained for both hydraulic conductivity and diffusion tests on different types of geotextile-enclosed GCLs and GCLs of different mass per unit areas. Petrov and Rowe (1997) showed that hydraulic conductivity values for GCLs with different permeants were related to the final bulk GCL void ratio and the nature of the permeating fluid. As will be shown below, sodium and chloride diffusion coefficients deduced for a GCL can also be related to the final bulk GCL void ratio for a given source solution.

The sodium and chloride diffusion coefficients deduced from the various tests are given in Table 3 and are plotted in Figs. 6 and 7 with respect to the final bulk GCL void ratio. The range of final bulk GCL void ratios tested was selected based on a typical range of final bulk GCL void ratios expected to be encountered in field
situations. Both sodium and chloride diffusion coefficients vary linearly with the final bulk GCL void ratio with almost an order of magnitude difference in diffusion coefficients from the lowest to the highest final bulk GCL void ratios considered. The $R^2$ values for a linear regression analysis through the points are 0.91 for chloride (Fig. 6) and 0.88 for sodium (Fig. 7). These $R^2$ values are considered to be good recognizing that three different types of GCL were tested and two different test methods were employed (CSD and SVD).
Test NWNWTC-CS was performed to simulate a GCL hydrating due to moisture from the underlying soil and then being subsequently consolidated due to the stress exerted during the placement of waste during landfill operations. Even though the sample was initially hydrated to a high bulk GCL void ratio under a 3 kPa stress and subsequently consolidated to a lower bulk GCL void ratio, the bulk GCL void ratio at which the diffusion test was performed ($e_B = 2.6$) controls the diffusion process and the data from this test falls on the relationship between the final bulk GCL void ratio and the sodium and chloride diffusion coefficients in Figs. 6 and 7. As shown by Petrov and Rowe (1997), the main effect of post-confinement stress application (applying a higher stress to the GCL than under which it was initially hydrated) is that it gives a higher final bulk GCL void ratio after consolidation than would have been realized if the full stress had been applied before hydration. This may be due to the fabric of the clay being developed in a more random fashion when hydrated at lower stresses and a higher stress is required to create the more orientated, lower void ratio fabric developed by pre-confinement hydration.

Based on the regression analysis given in Figs. 6 and 7 a simple equation can be written for the diffusion coefficient, $D_i$, in terms of final bulk GCL void ratio, $e_B$, viz:

$$D_i(\text{Cl}^-) = (1.18 e_B - 0.78) \times 10^{-10} \text{ m}^2/\text{s}, \quad \text{for } 1 < e_B < 3.5,$$

$$D_i(\text{Na}^+) = (1.82 e_B - 1.06) \times 10^{-10} \text{ m}^2/\text{s}, \quad \text{for } 1 < e_B < 3.5.$$

However it is important to note that this relationship was only established for source solutions of NaCl of less than 5 g/L (0.08 M). These results will be discussed further in the paper.

### 3.2. Effect of different contaminant source solutions

The relationships given by Eqs. (2) and (3) and shown in Figs. 6 and 7 were for hydration with distilled water and diffusion with 3 to 5 g/L (0.05 to 0.08 M) NaCl solutions. To investigate if these relationships are dependent on the source solution characteristics, diffusion tests were also performed with higher NaCl salt concentrations and a synthetic municipal solid waste leachate as described below.

#### 3.2.1. Effect of higher NaCl concentrations

To examine the effect of higher NaCl concentrations on the diffusion of sodium and chloride ions through bentonite, a five-phase specified volume diffusion test (test GB5PH) was performed at a 7.1 mm height using a granular bentonite (5500 g/m$^2$) taken directly from the NWNWT and WNWT GCLs. Bentonite was used alone to allow an examination of the general relationship between bentonite void ratio and increasing NaCl concentration that was independent of the type of GCL.

The first phase of diffusion testing was performed with a 4.6 g/L (0.08 M) NaCl solution. To examine the effect of the chemical composition of the receptor solution after the first phase, the depleted source solution was removed and replaced with another 4.6 g/L NaCl solution (phase II). The granular bentonite sample used for the first phase remained in the apparatus and the receptor reservoir fluid at the end of
phase I was used as the receptor fluid for the beginning of phase II. A second diffusion test was performed and diffusion coefficients were again obtained for sodium and chloride. The depleted source was then removed and replaced by a higher NaCl concentration solution, a diffusion test conducted and diffusion parameters deduced. In total, five tests were conducted with the same sample at the same bentonite void ratio as indicated in Table 4.

In phase I, the initial chloride and sodium concentrations in the receptor were in equilibrium with the initial porewater chemistry of the hydrated GCL and had values of approximately 0 c₀ and 0.27 c₀, respectively (with sulphate providing the charge balance). Thus the initial concentration gradient across the sample for Cl⁻ (0.14 c₀/mm) was 40% greater than for sodium (0.1 c₀/mm) in phase I. In phase II the normalized concentrations in the receptor at the start of the test (relative to the corresponding phase II source concentrations c₀) were approximately 0.27 c₀ and 0.33 c₀ for chloride and sodium respectively. The initial concentration gradient for chloride (0.1 c₀/mm) was only 6% greater than for sodium (0.094 c₀) and hence the two initial gradients were much closer than in phase I even though the composition of the source solution was the same in both cases. In phase III the normalized initial receptor concentrations were very close at approximately 0.13 c₀ and 0.14 c₀ for Cl⁻ and Na⁺ respectively while in phase IV and V the normalized initial receptor concentrations of Cl⁻ and Na⁺ were practically identical. As will become evident in later discussions, the initial concentration in the receptor and sample (relative to the source) has an effect on the diffusion coefficient for the GCLs tested. By inference, the porewater chemistry of the soil adjacent to a GCL in a field application may also initially influence diffusion through the GCL. This is consistent with Rowe (1998) who states that $D_e$ is really a mass transfer coefficient depending on things such as complex electrochemical gradients and therefore the contaminant transport model used in this paper will correctly model the tests provided initial parameters are correctly defined for each situation.

As can be seen from the results in Table 4, the repetition of the diffusion test in phases I and II gave slightly different deduced diffusion coefficients for both sodium and chloride. In particular in phase I the deduced diffusion coefficient for chloride is only 68% of that for sodium whereas in phase II the chloride diffusion coefficient has

<table>
<thead>
<tr>
<th>Phase</th>
<th>Concentration of NaCl used as $c_0$ (g/L)</th>
<th>Chloride diffusion coefficient, $D_c$ (m²/s)</th>
<th>Sodium diffusion coefficient, $D_s$ (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>4.6</td>
<td>$1.5 \times 10^{-10}$</td>
<td>$2.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>II</td>
<td>4.6</td>
<td>$1.9 \times 10^{-10}$</td>
<td>$2.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>III</td>
<td>9.1</td>
<td>$2.2 \times 10^{-10}$</td>
<td>$2.3 \times 10^{-10}$</td>
</tr>
<tr>
<td>IV</td>
<td>35.1</td>
<td>$3.8 \times 10^{-10}$</td>
<td>$3.8 \times 10^{-10}$</td>
</tr>
<tr>
<td>V</td>
<td>114.3</td>
<td>$4.2 \times 10^{-10}$</td>
<td>$4.2 \times 10^{-10}$</td>
</tr>
</tbody>
</table>
increased (relative to phase I) and that for sodium has decreased (relative to phase I) such that for phase II the deduced chloride diffusion coefficient is 95% of that for sodium. This demonstrates the potential influence of electrochemical interactions on deduced diffusion coefficients and will be discussed later in the paper. Phase III represents a doubling of NaCl concentration relative to that used in phases I and II and the diffusion coefficients for chloride and sodium increased by 15% relative to phase II. This small increase may be due to double layer contraction resulting from the increased NaCl concentration of the pore fluid as well as a reduction in the concentration of SO$_4^{2-}$ relative to Cl$^-$ and additional depletion of SO$_4^{2-}$ ions in the receptor fluid due to sampling. Phase IV represents a salt concentration similar to that of seawater. The diffusion coefficient for chloride and sodium subsequently increased by 73% and 65% compared to phase III respectively, probably the result of a combination of double layer contraction and c-axis contraction as shown by Petrov and Rowe (1997). For phase IV the diffusion coefficient for Cl$^-$ and Na$^+$ were the same. Increasing the salt content similar to that of a concentrated brine solution in phase V resulted in 10% higher deduced diffusion coefficients compared to phase IV for both sodium and chloride and again the two diffusion coefficients were the same. Test GB5PH chloride diffusion coefficients are plotted on Fig. 8 to illustrate the possible effects of different source solution concentrations on diffusion coefficients and how higher salt contents may affect relationships such as those in Figs. 6 and 7. To allow a direct comparison of the chloride diffusion coefficients given in Table 3 with those obtained for test GB5PH, it is appropriate to plot results in terms of bentonite void ratio.

Fig. 8. Change in chloride diffusion coefficient, $D_t$, due to increases in NaCl concentration.
void ratio (rather than of bulk GCL void ratio) since there are no geotextiles in test GB5PH. The regression line on Fig. 8 is based only on the diffusion coefficients used for Fig. 3 and does not depend on the results of test GB5PH.

If a soil remains saturated and occupies the same volume in a specified volume diffusion test, the bentonite void ratio of GB5PH remains constant. However Fig. 8 shows that the deduced chloride diffusion coefficient increases with increases in NaCl concentration. The changes from phase I to phase II are considered to be due to the relative changes in gradients for chloride and sodium. This is discussed in a later section of the paper. When the NaCl concentration increases from 9.1 g/L (0.16 M) to 114.3 g/L (2 M), the chloride and sodium diffusion coefficients almost double. Thus the relationship developed in Fig. 6 for 3 to 5 g/L (0.05 to 0.08 M) NaCl solutions is not applicable for substantially higher NaCl concentrations suggesting that any relationship between diffusion coefficients and final bulk GCL void ratio or bentonite void ratio is only valid for similar hydration and permeating conditions.

The results given here represent the worst possible situation since the void ratio is constrained to remain constant but the vertical stress between the bentonite and walls of the apparatus decreases with increasing NaCl concentration. For a GCL in a landfill base liner situation, one would expect that the effective stress on the GCL would remain relatively constant but that the final bulk GCL void ratio would decrease due to osmotic consolidation and/or c-axis contraction. For example, Fernandez and Quigley (1991) showed that the effective stress prevented some increase in hydraulic conductivity of a clay sample when permeated with certain hydrocarbon fluids.

To investigate the influence of effective stress and increasing salt contents on GCL diffusion coefficients as the NaCl concentration increases, test NWNWD-CS was performed with an NWNWT GCL at a constant stress of 145 kPa. Details and results of NWNWD-CS are given in Table 5 and results are plotted on Fig. 8 for comparison

<table>
<thead>
<tr>
<th>Phase</th>
<th>Concentration of NaCl used as $c_0$ (g/L)</th>
<th>Chloride diffusion coefficient, $D_1$ (m$^2$/s)</th>
<th>Sodium diffusion coefficient, $D_i$ (m$^2$/s)</th>
<th>Final bulk GCL void ratio, $e_B$ (−)</th>
<th>Bentonite total porosity, $n_i$ (−)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Spiked*</td>
<td>$1.5 \times 10^{-10}$</td>
<td>$1.5 \times 10^{-10}$</td>
<td>1.8</td>
<td>0.68</td>
</tr>
<tr>
<td>II</td>
<td>4.6</td>
<td>$1.5 \times 10^{-10}$</td>
<td>$1.6 \times 10^{-10}$</td>
<td>1.8</td>
<td>0.68</td>
</tr>
<tr>
<td>III</td>
<td>9.1</td>
<td>$1.6 \times 10^{-10}$</td>
<td>$1.7 \times 10^{-10}$</td>
<td>1.8</td>
<td>0.68</td>
</tr>
<tr>
<td>IV</td>
<td>35.1</td>
<td>(begin) $2.0 \times 10^{-10}$ (end) $1.9 \times 10^{-10}$</td>
<td>(begin) $2.0 \times 10^{-10}$ (end) $1.9 \times 10^{-10}$</td>
<td>(begin) 1.7 (end) 1.5</td>
<td>(begin) 0.68 (end) 0.65</td>
</tr>
<tr>
<td>V</td>
<td>114.3</td>
<td>(begin) $2.2 \times 10^{-10}$ (end) $2.1 \times 10^{-10}$</td>
<td>(begin) $2.2 \times 10^{-10}$ (end) $2.1 \times 10^{-10}$</td>
<td>(begin) 1.5 (end) 1.4</td>
<td>(begin) 0.65 (end) 0.63</td>
</tr>
</tbody>
</table>

*Notes: For phase I, the distilled water in the source reservoir used to hydrate the GCL (0.4 g/L Na$^+$ and 0.8 g/L SO$_4^{2-}$) was spiked with NaCl to establish equal gradients of Na$^+$ and Cl$^-$ through the sample initially ($c_0$ of Cl$^-$ 2.8 g/L, $c_0$ of Na$^+$ 2.2 g/L).

For phases IV and V, the sample deformed during testing and therefore two values of diffusion coefficients are given corresponding to parameters deduced at both the beginning and end of the test.
with GBPH5 (a SVD test). Phase I of this test was performed slightly different than GB5PH to examine the influence of initial gradients on chloride and sodium diffusion coefficients. Instead of placing only 1 cm of deionized, distilled water in the source solution to hydrate the GCL, deionized, distilled water of the same volume as an NaCl solution used to perform a diffusion test was added to the source to hydrate the sample. After hydration of the GCL, the hydration fluid in the source and receptor was sampled and analyzed for major ions to ensure chemical equilibrium. A concentrated NaCl solution was then made to spike this source fluid at the beginning of the test. The dilution of the concentrated NaCl solution into the hydration fluid was such that initial concentrations in the source were 2.2 g/L of Na\(^+\), 0.8 g/L of SO\(_4\)\(^{2-}\) and 2.8 g/L of Cl\(^-\). Initial receptor concentrations of 0.4 g/L of Na\(^+\), 0.8 g/L of SO\(_4\)\(^{2-}\) and approximately 0 g/L of Cl\(^-\) resulted in gradients of 0.14 c\(\text{m}^2/\text{s}\) for both sodium and chloride. As one can see from Table 5, both sodium and chloride deduced diffusion coefficients are the same for phase I (1.5 \(\times\) 10\(^{-10}\) m\(^2\)/s). For phase II, the source fluid was removed entirely and replaced with a 4.6 g/L (0.08 M) NaCl solution. With some sulphate ions still remaining in the receptor after phase I, the initial concentration of sodium in the receptor (0.32 c\(\text{m}^2/\text{s}\)) was slightly greater than chloride (0.26 c\(\text{m}^2/\text{s}\)), resulting in a slightly higher sodium diffusion coefficient (1.6 \(\times\) 10\(^{-10}\) m\(^2\)/s) compared to that of chloride (1.5 \(\times\) 10\(^{-10}\) m\(^2\)/s). Phase III showed the chloride diffusion coefficient (1.6 \(\times\) 10\(^{-10}\) m\(^2\)/s) to be slightly less than that of sodium (1.7 \(\times\) 10\(^{-10}\) m\(^2\)/s), however both increased slightly relative to phase II results. Increasing NaCl concentrations in Phase IV (35.1 g/L; 0.6 M) and Phase V (114.3 g/L; 2.0 M) resulted in higher sodium and chloride diffusion coefficients compared to the previous three phases as shown in Table 5. For each of these two phases, Na\(^+\) and Cl\(^-\) diffusion coefficients were the same for the reasons discussed for test GB5PH.

Comparing Tables 4 and 5 and looking at Fig. 8, diffusion coefficients for NWNWD-CS were much lower compared to the specified volume, GB5PH test at higher NaCl concentrations. This suggests that application of effective stress on a GCL may be beneficial at reducing increases in diffusion coefficients for concentrated NaCl solutions (0.6 M and 2 M). However, for NWNWD-CS, even though the change in diffusion coefficient from phase I (1.4 \(\times\) 10\(^{-10}\) m\(^2\)/s) to phase V (2.2 \(\times\) 10\(^{-10}\) m\(^2\)/s), was not that large, the increasing salt content caused the bentonite void ratio to decrease from 2.2 to 1.7 (see Fig. 8). If Eq. (2) is used to predict the chloride diffusion coefficient for a bulk GCL void ratio of 1.4 (NWNWD-CS, end of phase V), the value predicted (0.88 \(\times\) 10\(^{-10}\) m\(^2\)/s) is approximately 150% lower than what was observed for phase V (2.2 \(\times\) 10\(^{-10}\) m\(^2\)/s). Therefore the change in chloride diffusion coefficient is more than it initially appears if one compares the expected diffusion coefficient at the lower void ratio. However, the ultimate magnitude of diffusion coefficient is still much lower for the 2.0 M NaCl solution for the CSD test compared to the SVD test when both samples started at similar void ratios.

To investigate if this deformation during diffusion testing had any influence on the modelling these tests, the parameters at both the beginning and end of each phase were used to deduce diffusion coefficients. Table 5 shows there is very little difference in the deduced diffusion coefficients for these two possible cases.
The important point to be made here is that the deduced diffusion coefficient depends both on the void ratio and the level of potential interaction of the leachate with the bentonite under the anticipated field conditions and hence tests should be performed using a leachate, receptor solutions and applied stress conditions as close as practical to that anticipated in the field application.

3.2.2. Effect of synthetic leachate

Compared to the NaCl solutions above, the complex electrochemical synthetic leachate solution shown in Table 2 has many different ions that may cause many different levels of ion exchange, double layer contraction, or c-axis contraction to occur during GCL diffusion testing. Synthetic leachate was chosen to simulate a realistic application for a GCL, although it is acknowledged that many other harsher solutions could have been used to examine the effect of factors such as ion exchange. Table 3 shows that for test NWNWT6-SV, the chloride diffusion coefficient of $2.2 \times 10^{-10} \text{ m}^2/\text{s}$ is substantially higher than the value of $1.5 \times 10^{-10} \text{ m}^2/\text{s}$ obtained for test NWNWT1-SV or $1.4 \times 10^{-10} \text{ m}^2/\text{s}$ for test NWNWT5-SV using the same type of GCL and similar final bulk GCL void ratios. It is similar to that in phase III of GB5PH. Thus the different source solution chemistry appears to have increased the diffusion coefficient deduced based on total porosity by almost 50% for chloride (see Fig. 9).

Often in landfill base liner applications an effective stress will be present as leachate migrates through the GCL. Tests NWNWE-CS and NWNWF-CS (Table 3) show chloride diffusion results for the synthetic leachate solution at stresses of 22 kPa and 145 kPa respectively. It should be noted that negligible deformation of NWNWE-CS ($e_B = 2.6$) took place during diffusion testing while sample NWNWF-CS reduced 0.4 mm in height during diffusion testing ($e_{B_{start}} = 1.8; e_{B_{end}} = 1.6$). Therefore the
range of deduced chloride diffusion coefficients for NWNWF-CS for both the initial and final sample parameters are given on Fig. 9. Again, both results plot above the regression line from Fig. 6 obtained for NaCl concentrations of less than 5 g/L (0.08 M) and the result for the CSD test (145 kPa) is very similar to that obtained from the SVD test. It can be hypothesized that the deviation of the Cl results for NWNW6-SV (SVD test) from the 0.08 M NaCl solutions may have been influenced more by the complex interaction of varying gradients for the leachate compared to the 0.08 M NaCl solution than a decrease in effective pore space due to double layer contraction.

It should be noted that no diffusion coefficient is given for sodium in Table 3 (Test NWNWT6-SV). As other cations in the synthetic leachate solution migrate through the clay, they undergo cation exchange. Because Na$^+$ is the dominant ion on the clay exchange sites, some Na$^+$ will be desorbed as the leachate travels through the GCL. No fit to the experimental data can be obtained using a single contaminant transport model if desorption is a predominant mechanism influencing transport.

3.3. Effect of type of GCL manufacture

Three different types of GCL manufacture were tested in this study (Table 1). The NWNWT and WNWT GCLs are similar, except that they employ a different bottom geotextile, while the WNWBT GCL is similar to the WNWT GCL except that it has powdered bentonite in the middle and, more significantly, sprinkled on the top of the GCL. In a companion paper, Lake and Rowe (2000) showed that for confining stresses above about 100 kPa, the three GCLs swelled to similar bulk GCL void ratios for similar confining stresses. The NWNWT and WNWT GCLs exhibited similar swelling behavior at all stresses but below 100 kPa the WNWBT GCL swelled to much higher bulk GCL void ratios. It is interesting to revisit Figs. 6 and 7 to examine if there is any apparent effect of the type of GCL manufacture on deduced GCL diffusion coefficients.

As mentioned earlier, the results in Figs. 6 and 7 show a linear relationship for all the samples tested with 3 to 5 g/L NaCl solutions. This in itself suggests that for the three GCLs and range of bulk GCL void ratios examined, the type of GCL manufacture has little practical effect on deduced GCL diffusion coefficients. If Figs. 6 and 7 are examined closely, there appears to be less scatter of chloride and sodium diffusion coefficients at lower final bulk GCL void ratios than at higher bulk GCL void ratios. However, there is no pronounced trend of one type of GCL having a higher diffusion coefficient than another. Based on the results of Lake and Rowe (2000), one would expect that if any GCL were to deviate from the relationship in Figs. 6 and 7, it would be the WNWBT GCL. However, relative to the scatter that is present at higher bulk GCL void ratios, this does not appear to be the case. The thermally treated needlepunching of the WNWBT GCL can be expected to restrict the bulk void ratio of the bentonite core at higher bulk void ratios, even though the powdered bentonite on the surface of the cover geotextile is allowed to swell unconfined. Thus it can be inferred that the thermally treated needle punching restricted swelling of the core of these GCLs and it may be anticipated that this will control the diffusion
through the GCL at the lower confining stresses examined. The powdered surface bentonite may swell and occupy part of the volume but it apparently does not control diffusion.

The fact that the level of restraint in the core can have a significant influence on the results is evident from the results presented by Lake and Rowe (2000) who examined two similar WNW GCLs but where one GCL was thermally treated and needlepunched while the other was only needlepunched. When subjected to a CSD test at 3 kPa with a 4.6 g/L NaCl solution, the non-thermally treated GCL swelled to a higher bulk GCL void ratio (8.2 versus 4.7) and yielded higher sodium and chloride diffusion coefficients than the thermally treated GCL. Apparently the thermal locking of the needlepunched fibres had restricted the bulk GCL void ratio of the thermally treated GCL during hydration at 3 kPa, resulting in lower GCL diffusion coefficients. The effect of thermally treated needlepunching also was apparent from post-test inspections of diffusion test samples listed in Table 3. The samples at the 5.6 mm and 7.1 mm heights were very flat along the bottom and top, with measured heights by a vernier caliper were the same as the ring heights (i.e. 5.6 mm and 7.1 mm). At the 9.1 mm and 11.0 mm heights, even though the measured heights were again the same as the ring height, the bottom of some of the GCLs were “dimpled”. In other words the fibres were preventing local areas of the GCL from swelling to the height of the ring. Therefore, even though the GCLs were the desired heights, localized portions of the GCLs were at slightly smaller heights (i.e. smaller void ratios). At the 9 mm height, the effect was not as great as at the 11 mm height but was present nevertheless. Some samples may be affected by this more than others depending on factors such as the mass per unit area of the bentonite in the GCL, the amount of bonding between the fibres and the bottom geotextile, and the density of the needlepunched fibres. This may be a cause of some of the scatter in the deduced diffusion coefficients reported in Figs. 6 and 7 at higher bulk GCL void ratios.

3.4. Constant stress versus specified volume diffusion testing

To examine the effect of the type of diffusion test performed, two different approaches were used: 1) control the final bulk GCL void ratio during diffusion testing (SVD), or 2) control the stress conditions during diffusion testing (CSD). A control over the final bulk GCL void ratio allows a comparison of diffusion coefficients for different types of GCLs regardless of the stresses generated by the bulk GCL void ratio. A control over the confining stress applied during diffusion testing allows comparison of diffusion test results under similar stress conditions (but different void ratios for different GCLs). The CSD test has the added benefit that one can monitor the GCL height during hydration and diffusion testing under the specified confining stress.

Three CSD tests were performed as indicated in Table 3. Tests NWNWTA-CS and NWNWTB-CS were conducted on specimens hydrated and maintained under the noted applied stress. In test NWNWTC-CS, the GCL was allowed to hydrate under a low stress condition (3 kPa) and it was then consolidated under a higher stress (145 kPa) before starting the diffusion test. This was an attempt to simulate a situation that
may occur when a GCL becomes hydrated under relatively low stress conditions and then is subsequently consolidated due to the stresses from overlying waste as a landfill is filled.

As previously noted, all the results in Table 3 are consistent with the linear relationship shown in Figs. 6 and 7 regardless of the test method (CSD or SVD) with both tests yielding similar diffusion coefficients at a similar bulk GCL ratio.

Deformation data for test NWNWTC-CS showed that during the course of the diffusion test, the sample decreased in height by almost 0.4 mm with the majority of the deformation occurring after the first day of diffusion testing. This was probably due to a combination of double layer contraction and a relatively high bulk void ratio from being hydrated under 3 kPa stress conditions and subsequently consolidated to 145 kPa. To examine the results of NWNWTC-CS, it is useful to plot the bulk GCL void ratio at the beginning of diffusion testing and the lower bulk GCL void ratio at the end of the test as shown by diamond symbols on Fig. 9. Although the bulk GCL void ratio did change slightly during diffusion testing, the magnitude of the change was small and both bulk GCL void ratios and corresponding diffusion coefficients from this test plot close to the linear relationship established from the other tests.

3.5. Comparison of chloride and sodium diffusion coefficients

Even with the relatively simple NaCl source solutions utilized for the tests in this paper, Na\(^+\) and Cl\(^-\) ions do not necessarily move together through the system to maintain charge balance. This is because the hydrated bentonite contains a significant concentration of Na\(^+\) and SO\(_4^{2-}\) ions (see Rowe et al., 2000). Thus during hydration, the Na\(^+\) and SO\(_4^{2-}\) ions from the bentonite in the GCL diffused into the receptor reservoirs (that initially contained distilled water) until chemical equilibrium was reached between the GCL and the receptor reservoirs. When the source solution of sodium chloride is placed above the hydrated GCL, the concentration gradient of Cl\(^-\) is higher than that of Na\(^+\) and there is also some back-diffusion of SO\(_4^{2-}\) ions from the soil porewater and receptor solution into the source. This means that the Na\(^+\) and Cl\(^-\) ions may not migrate at the same rate through the system. As discussed by Kemper and van Schaik (1966), Yeung and Mitchell (1992) and Rowe et al. (1995), the movement of ions involves several components (i.e. true diffusion, electrical flow, and bulk flow) and in particular, electrical flow may influence the sodium and chloride diffusion coefficients deduced for a particular test.

In a system where the source solution was NaCl and no other diffusion was significant, the change in the normalized source concentrations of Na\(^+\) and Cl\(^-\) with time should be identical to maintain a charge balance. However, inspection of Figs. 3 and 4 indicates that this is not the case and the drop in the concentration of Cl\(^-\) in the source is greater than the drop in Na\(^+\). Here charge balance is maintained by the upward diffusion of SO\(_4^{2-}\) and in order to satisfy charge balance in the source at any given time one must include consideration of the concentration of SO\(_4^{2-}\) in the source at that time.

Comparing the initial concentration gradient between the source and receptor (eg. Figs. 3 and 4), it is found that the gradient for chloride is much greater than for sodium
(due to initial receptor concentrations of $\sim 0$ and 0.25 $c_0$, respectively). As a consequence, the initial gradient for chloride is 33% greater than for sodium. However, the need to maintain electrical charge balance means that chloride must, in essence, pull sodium with it and increase the porous media diffusion coefficient ($D_n = n_1D_s$) of sodium while in turn, sodium is retarding the movement of chloride (reducing the porous media diffusion coefficient of chloride). As a consequence, for the tests reported in Table 3, the Na$^+$ diffusion coefficients are higher than Cl$^-$ diffusion coefficients (see Table 3) even though at infinite dilution in free solution the opposite would be true.

Additional evidence relating to the effect of the electrical interaction of ions on the deduced diffusion coefficients is given by the results of test GB5PH (Table 4). As mentioned previously, phase I is similar to the other tests reported in Table 3 in that initially the gradient for chloride is substantially greater than for sodium. This explains why the deduced diffusion coefficients for sodium and chloride in phase I are consistent with those reported in Table 3. However, after phase I has been completed the mass of SO$_4^{2-}$ in the receptor has been depleted due to sampling and more importantly, the concentration of chloride in the receptor at the end of phase I has increased enough to almost provide a charge balance for Na$^+$ in the receptor (still some SO$_4^{2-}$). The gradient of chloride at the start of phase II is only 6% greater than that for sodium and there is a greater need for a similar molar flux to diffuse from the source to the receptor to maintain charge balance. Thus the deduced sodium diffusion coefficient decreases while the deduced chloride diffusion coefficient increases and the ratio of chloride to sodium diffusion coefficients increases from 0.68 in phase I to 0.95 in phase II. Although the difference in diffusion coefficients between phase I and II is not great, it emphasizes the role that electrical interactions play with respect to diffusion through soil.

Since the initial concentration of Na$^+$ in the receptor is controlled by the bentonite porewater chemistry, one would expect that the difference between Na$^+$ and Cl$^-$ would become smaller as the source concentration was increased relative to the background concentration. As a consequence, one would expect that as the NaCl source concentration increased, the molar flux and the diffusion coefficient for Cl$^-$ and Na$^+$ would tend to the same value (to ensure charge balance). This was evident for the results given in Table 4. Sodium and chloride diffusion coefficients were also the same value for phase I of test NWNWD-CS (Table 5) when there was no concentration difference of SO$_4^{2-}$ across the sample due to the hydration procedure and similar initial gradients of Na$^+$ and Cl$^-$ across the sample as explained in Section 3.2.1. This clearly illustrates the need for caution in using published diffusion coefficient results at infinite dilution in free solution for real systems and emphasizes the fact that the “diffusion” coefficient deduced from typical tests on soil are really mass transfer coefficients rather than true diffusion coefficients since they incorporate the effect of factors in addition to true molecular diffusion (Rowe et al., 1995).

It should be noted again that the diffusion coefficients ($D_1$) reported in this paper represent mass transfer coefficients deduced using the total porosity. The actual effective diffusion coefficient of both sodium and chloride may also be affected by anion exclusion. It should be recognized that the use of the total porosity $n_1$ and the corresponding value of $D_1$ given in Table 3 represent a convenient way of modeling...
transport through a GCL and these parameters do not necessarily represent the true effective values. However, they do provide a reasonable estimate of the porous media diffusion coefficient, \( D_p \), and can be used to establish mass transfer across a single GCL.

3.6. Diffusion considerations when designing GCL landfill liner systems

In the design of waste containment systems with GCLs, it would be desirable to have a relationship between the stress levels expected at a waste containment facility and the corresponding diffusion coefficient. However, as shown throughout this paper there are many different variables that interact with the GCL system such as the type of contaminant source solution, GCL hydration conditions, and type of GCL. Although the stress present on a liner system and the diffusion coefficient may be related for a given GCL and contaminant source, this relationship may change if the contaminant source or hydrating conditions change which may cause changes in the void ratio of the bentonite. Barbour and Fredlund (1989) discussed how the results of consolidation tests performed on a Na\(^+\) montmorillonite at different salt concentrations exhibited different void ratios at the same stress level and hence different e-log p curves. This is because when comparing the same stress levels, higher salt contents caused increasing amounts of osmotic consolidation.

The preferred means of obtaining diffusion coefficients is to perform a test under conditions as close as practical to those expected in the field (i.e. under similar hydration conditions, applied stress and source contaminant). However, when no diffusion data is available for initial calculations and the contaminating solution behaves similar to the 3–5 g/L (0.05 M to 0.08 M) NaCl solutions examined in this paper, an initial estimate of chloride diffusion coefficients can be made as described below. Readers are cautioned that the nature of contaminant source solution may alter the diffusion coefficients and give rise to values that are different than those that would be deduced from what is described below.

Chloride is commonly used as a tracer contaminant in landfill design (see Rowe et al., 1995; Ontario Ministry of Environment (MOE), 1998). Thus if one is interested in performing contaminant transport analyses for chloride, an estimate of the final bulk GCL void ratio can be made using swell data. For example if one considers a NWNWT GCL with a vertical stress of approximately 150 kPa (assuming the GCL is hydrated with water under this applied stress), one can use the pre-confinement swell data in Fig. 10a to deduce a bulk GCL void ratio of approximately 1.9. Fig. 11 shows that for a NWNWT final bulk GCL void ratio of 1.9, the chloride porous media diffusion coefficient will be approximately \( D_p = 1.0 \times 10^{-10} \) m\(^2\)/s. As explained earlier, for a single GCL layer similar to those tested, the movement of the contaminant through the GCL is controlled by \( D_p = nD \). However for most contaminant transport modeling a value of the porosity, \( n \), and diffusion coefficient, \( D \), are needed as inputs. Since it has been shown that transport through a single GCL is insensitive to the precise values of \( n \) and \( D \) (provided that the product is equivalent to \( D_p \)), one can estimate \( D_i = D_p/n_i \) where reasonable values of \( n_i \) are given in Fig. 11 for a range of GCL bulk void ratios. In this example, for \( e_B = 1.9 \), a reasonable value of \( n_i \) is 0.7 as given in Fig. 11. Alternatively a value of \( n_i \) can be deduced for the specific value of
Fig. 10. NWNWT GCL swell data reproduced from Lake and Rowe (2000).

Pre-Confinement Stress Application (Hydrated with Distilled Water)

NWNWT GCL

\[ e_B = -1.59 \log(\sigma) + 5.33 \]
For 5 kPa < \( \sigma \) < 400 kPa

(a)

Post-Confinement Stress Application (Hydrated with Distilled Water)

NWNWT GCL

(b)

Stress, \( \sigma \) (kPa)
and GCL properties as described in Appendix A. For $n_t = 0.7$, the resultant diffusion coefficient, $D_t$, will be approximately $1.5 \times 10^{-10}$ m$^2$/s.

If the situation discussed above was varied such that the NWNWT GCL swelled under low stress conditions (say 6 kPa), and was then consolidated under a 150 kPa stress due to the overlying waste, the final bulk GCL void ratio could be estimated from the post-confinement swell data for the NWNWT GCL in Fig. 10b to be approximately 2.8. Using Fig. 11, a chloride porous media diffusion coefficient of $2.0 \times 10^{-10}$ m$^2$/s and bentonite total porosity of 0.75 can be estimated for these conditions. This implies a diffusion coefficient of $D_t = 2.6 \times 10^{-10}$ m$^2$/s.

Table 3 shows that a chloride diffusion coefficient, $D_t$, of $2.2 \times 10^{-10}$ m$^2$/s was obtained from the testing program for test NWNWT6-SV (synthetic leachate). This test can be used to emphasize the potential dangers of using Fig. 11 data (developed from 0.08 M NaCl solutions) for predicting chloride diffusion coefficients for a synthetic leachate. NWNWT6-SV had a bulk GCL void ratio, $e_B$, of 1.9, a bentonite total porosity, $n_t$, of 0.70 and a chloride diffusion coefficient, $D_t$, of $2.2 \times 10^{-10}$ m$^2$/s. However if Fig. 11 is used to try to predict the Cl$^-$ diffusion coefficient for this synthetic leachate test, a higher Cl$^-$ diffusion coefficient is predicted. By taking the bulk GCL void ratio as 1.9, the corresponding porous media diffusion coefficient, $D_p$, can be estimated from Fig. 11 as $1.2 \times 10^{-10}$ m$^2$/s. Since the test was performed at a bentonite total porosity of 0.70, the resultant diffusion coefficient, $D_t$, is therefore estimated as $1.6 \times 10^{-10}$ m$^2$/s (using Fig. 11 and the same procedure as described in the previous paragraph), which is almost a 40% below what was actually experimentally measured ($2.2 \times 10^{-10}$ m$^2$/s).

If one is interested in estimating sodium diffusion coefficients in a similar manner, Fig. 12 can be used in a similar way to Fig. 11 for chloride to establish GCL diffusion coefficients for sodium.
Fig. 12. Typical values of total porosity and sodium porous media diffusion coefficients for bulk GCL void ratios.

The initial clay fabric is known to influence the hydraulic conductivity of a soil when permeated with various fluids. Various researchers (Mesri and Olsen, 1971; Fernandez and Quigley, 1985; Kenney et al., 1992; Petrov and Rowe, 1997) have shown that soils initially hydrated with concentrated salt solutions or pure organic fluids will exhibit a more flocculated fabric and hence larger effective pore space than soils with a dispersed fabric at a given void ratio resulting in a higher hydraulic conductivity than soil initially hydrated with water. Various factors such as effective stress, type of clay mineral, and type of hydrating medium will influence the relative magnitude of difference. Results presented in Table 3 were performed for GCL samples hydrated with distilled water and hence represent a more dispersed clay fabric compared to the possibility of samples being hydrated with a concentrated salt solution or leachate. Therefore there is a possibility that samples hydrated with a concentrated salt or leachate may have a more flocculated clay fabric, larger effective void space and hence higher diffusion coefficient values. As shown by Daniel et al. (1993), whether or not GCLs, when constructed, will remain “dry” before coming in contact with these solutions is dependent on factors such as the suction potential of underlying soils. Daniel et al. (1993) examined the hydration characteristics of the bentonite component of GCLs and found that for a GCL placed in on a soil close to the wilting point (1500 kPa suction) the GCL reached a moisture content of 50%. For a moist soil (suction between 0 and 100 kPa), the moisture content equilibrated to 100% and 140% with a hydration time of approximately one to three weeks. Hydraulic conductivity measurements showed that hydraulic conductivity values of the GCL when permeated with pure organic fluids were less than $10^{-11}$ m/s when the moisture content of the underlying soil was above 100%. Therefore it is likely that a GCL placed as part of a liner system in a landfill will undergo some hydration after
placement of a cover soil and any “first” contact with a leachate will be with a GCL partially or fully hydrated from the contacting soils. If the GCL was to be placed in an arid environment, there may have to be allowances made for pre-hydrating the GCL with water (with an effective stress applied) and preventing the GCL from desiccation until such a time that the leachate is expected to come into contact with the GCL.

4. Conclusions

The diffusion of sodium and chloride through GCLs has been examined for a range of conditions including different final bulk GCL void ratios, different contaminant source solutions, different types of GCL, and different test methods. The following conclusions are applicable to the results presented in this paper but should not be generalized without additional investigation:

1. When considering similar hydration conditions, stress levels, and permeating fluids; the GCLs tested in this paper exhibited a linear relationship between final bulk GCL void ratios and diffusion coefficients. Even when a GCL was hydrated under low stress conditions and subsequently consolidated to a lower final bulk GCL void ratio, it was the bulk GCL void ratio during diffusion testing that controlled the diffusion parameters. Generally, the diffusion coefficient was shown to decrease as the bulk GCL void ratio decreased.

2. The diffusion coefficient may change with changing composition of the source reservoir solution and the linear relationship given in this paper only applies to NaCl solutions with 3 to 5 g/L (0.05 M to 0.08 M) concentrations.

3. At similar bulk GCL void ratios, there was no significant difference in diffusion coefficients obtained for the three GCLs examined in this study. However, there was some scatter of diffusion coefficients at higher bulk GCL void ratios that was attributed to the effect of the thermal treatment at low applied stresses.

4. At infinite dilution, the free solution diffusion coefficient of Na$^+$ is less than that of Cl$^-$. However the diffusion coefficient for Na$^+$ was greater than that for Cl$^-$ for most of the tests reported in this paper, primarily due to back diffusion of SO$_4^{2-}$ from the GCL and the lower gradients of Na$^+$ compared to Cl$^-$ at the start of the test.

5. Diffusion tests performed with high NaCl concentrations (up to 2 M) were compared by two different test methods, specified volume diffusion and constant stress diffusion tests. Application of an effective stress resulted in much lower absolute diffusion coefficients for 0.6 M and 2 M compared to the specified volume diffusion test. The combination of an effective stress and high NaCl concentrations caused contraction of the sample thickness, reducing the void ratio.

6. The diffusion coefficient of chloride for diffusion tests performed with synthetic leachate was greater than that observed for 0.08 M NaCl solutions. This increase was hypothesized to be due to a combination of increased effective pore space due to double layer contraction as well as the interaction of the many ions in the synthetic leachate as they migrate through the sample.
7. Because of the influences of hydration fluid, source reservoir solution and stress levels during diffusion testing, diffusion tests should attempt to simulate the conditions expected in the field. It is recommended that constant stress diffusion tests be performed to simulate the stress conditions expected in the field. Examples have been provided to illustrate how to obtain an initial estimate of the diffusion coefficient of chloride as well as an estimate of the total bentonite porosity normally required for contaminant transport modeling. A similar approach can be followed for sodium.

Acknowledgements

The research reported in this paper was funded by Terrafix Geosynthetics, the National Research Council of Canada (under the IRAP program), and by the Natural Sciences and Engineering Research Council of Canada. The authors very gratefully acknowledge the value of discussions with Messrs. Don Stewart and Cal Reaume of Terrafix and Mr. Kent von Maubeuge of Naue Fasertechnik during the preparation of this paper. Thanks are also extended to Ms. Leila Hrapovic and Mr. Jamie van Gulck for supplying the synthetic leachate. The information in this paper should not be used without independent examination and verification of its suitability for any particular project.

Appendix A. Definitions

The final bulk GCL void ratio, $e_B$, is defined by (Petrov et al., 1997):

$$e_B = \frac{H_{GCL} - H_s}{H_s},$$  \hspace{1cm} (A.1)

where $H_{GCL}$ is the GCL height and $H_s$ is the height of solids in the GCL and

$$H_s = H_{sBENT} + H_{sGEO}$$  \hspace{1cm} (A.2)

with

$$H_{sBENT} = \frac{M_{BENT}}{\rho_s(1 + w_0)},$$  \hspace{1cm} (A.3)

$$H_{sGEO} = \frac{M_{GEO}}{\rho_{sg}},$$  \hspace{1cm} (A.4)

where $H_{sBENT}$ is the height of bentonite solids; $H_{sGEO}$ is the height of geotextile solids; $M_{GCL} = M_{BENT} + M_{GEO}$ is the mass per unit area of the GCL; $M_{BENT}$ is the mass of bentonite per unit area in the GCL; $M_{GEO}$ is the mass of geosynthetics per unit area in the GCL (Typical values for the three GCLs examined are: NWNWT-620 g/m$^2$, WNW-390 g/m$^2$, WNWBT-500 g/m$^2$); $\rho_s$ is the density of bentonite solids (typical
value of 2.61 mg/m$^3$; $\rho_{sg}$ is the density of polypropylene geotextile solids (typical value of 0.91 mg/m$^3$); $w_0$ is the initial water content of the bentonite (typical value of 0.08).

The void ratio of the bentonite in the GCL is given by

$$e_{BENT} = \frac{H_{BENT} - H_{sBENT}}{H_{sBENT}}, \quad (A.5)$$

where $H_{BENT}$ is the height of bentonite in the GCL and is given by

$$H_{BENT} = H_{GCL} - H_{GEO}. \quad (A.6)$$

$H_{GEO}$ is the height of geotextiles in the GCL (this value is difficult to obtain accurately and therefore, based on a number of measurements the geotextile heights were taken as 1.1 mm for the NWNWT and WNWBT GCL and 0.8 mm for the WNWT GCL for all the GCLs examined in this paper).

For a given GCL, $H_{GCL}, H_{GEO}, w_0, M_{GCL}, M_{GEO}, \rho_s, \rho_{sg}$ are either measured or known and hence $e_{BENT}$ can be deduced from Eqs. (A.1)–(A.6) and the total porosity of the bentonite, $n_t$, can be calculated from

$$n_t = \frac{e_{BENT}}{1 + e_{BENT}}, \quad (A.7)$$

In a consolidation or swell test, $e_B$ is deduced from Eqs. (A.1) and (A.2) based on known values of $H_{GCL}, M_{BENT}, M_{GEO}, \rho_s, \rho_{sg}$ and $w_0$. If $e_B$ has been estimated from charts such as Fig. 7 and $M_{GCL}, \rho_s, \rho_{sg}$ and $w_0$ can be measured or estimated for the GCL, then $H_{sBENT}$ can be deduced from Eq. (A.3) and $H_{GCL}$ can be deduced from Eq. (A.1). Thus $H_{BENT}$ can be deduced from Eq. (A.6) and $e_{BENT}$ and $n_t$ deduced from Eqs. (A.5) and (A.7), respectively.

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