

Investigation of the effects and degree of calcium exchange on the Atterberg limits and swelling of geosynthetic clay liners when subjected to wet–dry cycles

Abdelmalek Bouazza^{a,*}, Stephan Jefferis^{b,c}, Thaveesak Vangpaisal^d

^aDepartment of Civil Engineering, Monash University, Building 60, Melbourne, Vic. 3800, Australia

^bSchool of Engineering, University of Surrey, Guildford, Surrey GU2 7XH, UK

^cEnvironmental Geotechnics Limited, Oxford OX25 4AD, UK

^dUbon Ratchathani University, P.O. Box 3, Warin Chamrap, Ubon Ratchathani 34190, Thailand (Formerly Monash University)

Received 10 October 2005; received in revised form 29 October 2005; accepted 4 November 2006

Available online 20 December 2006

Abstract

In the field, particularly in landfill cover system applications, a geosynthetic clay liner may be exposed to inorganic cations such as calcium, magnesium and aluminium which can alter the performance of the GCL bentonite component especially if accompanied by drying and re-wetting as a result of seasonal changes in temperature and rainfall. To investigate the impacts of wetting and drying, the Atterberg limits of the GCL bentonite component and swelling of the GCL were determined under wet–dry cycling with calcium chloride solution used for the wetting cycles. From the quantities of calcium chloride added at each wetting stage, estimates were made of the degree of ion exchange of calcium for sodium on the clay. The authors recognise that there is a substantial literature on the effects of inorganic salts such as calcium chloride on the behaviour of bentonite. However, so far as they are aware, the results of such tests involving cation exchange have not been investigated in terms of the degree of exchange achieved.

In the tests two calcium chloride solutions were used: 0.0125 and 0.125 M. This allowed a detailed investigation of the effects of the degree of sodium–calcium exchange on the bentonite and some, though more limited, consideration of the effects of ionic strength of the pore fluid. It is shown that for Atterberg limit tests, even using 0.125 M calcium chloride solution, full calcium exchange could not be achieved as the amount of liquid added to bring the bentonite to the liquid or plastic limit did not contain sufficient calcium ion for full exchange. For the swell tests, much higher liquid-to-solid ratios were used so that near full exchange could be achieved though only after several wet–dry cycles. Using these data the paper develops a methodology for estimating the position of the cation exchange equilibrium and shows how complex this analysis can become. It also shows that on occasion only limited cation exchange may be achieved in laboratory tests whereas near full exchange may occur in the field. If the effects of full/near full exchange are to be investigated, laboratory procedures must be specially designed to achieve high degrees of exchange, for example, by using multiple exchange cycles, large liquid-to-solid clay ratios or by permeating the clay with the cation exchange liquid—though such permeation procedures may take a very substantial time.

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Keywords: Geosynthetic clay liners; Wet–dry cycles; Bentonite; Ion exchange; Atterberg limits; Swelling

1. Introduction

Geosynthetic clay liners are widely used in landfill applications and have been subject to considerable recent

research (e.g. Southen and Rowe, 2005; Barroso et al., 2006; Dickinson and Brachman, 2006; Hurst and Rowe, 2006; Bouazza and Vangpaisal, 2006; Touze-Foltz et al., 2006). They predominantly use natural sodium bentonite as the low-permeability element. The major clay mineral constituent of sodium bentonite is sodium montmorillonite. Typically, minor mineral components of natural bentonites include quartz, feldspars, carbonates and micas. The quality of bentonite tends to increase with increase in

*Corresponding author. Tel.: +61 3 9905 4956; fax: +61 3 9905 4944.

E-mail addresses: malek.bouazza@eng.monash.edu.au (A. Bouazza), egl@environmentalgeotechnics.com (S. Jefferis), thaveesak.v@ubu.ac.th (T. Vangpaisal).

montmorillonite content (Lee and Shackelford, 2005); high-quality bentonite contains usually 75–90% montmorillonite by mass (Egloffstein, 2002). Bentonite is a three-layer clay mineral of the smectite group. The basic three-layer structure consists of an alumina octahedral layer sandwiched between silica tetrahedral layers. As a result of substitutions in the mineral lattice and especially the alumina layer, montmorillonite has a high cation exchange capacity and these cations easily can be exchanged as they are weakly bound.

Experimental evidence shows that cation exchange can impair the self-healing capacity of sodium bentonite GCLs and their mechanical properties and consequently induce changes in hydraulic conductivity and gas permeability (James et al., 1997; Melchior, 1997, 2002; Mazzieri and Pasqualini, 2000; Lin and Benson, 2000; Bouazza et al., 2006; Touze-Foltz et al., 2006). Egloffstein (2001) noted that the time to complete cation exchange was influenced by a number of factors such as the type and the mass per unit area of bentonite, the nature and concentration of ions in the pore water and the quantity of infiltrating water.

This paper presents a detailed analysis of the effects of the degree of sodium–calcium exchange on a geosynthetic clay liner with consideration of the effects of ionic strength of the pore fluid. The study was part of a larger study on gas permeability of GCLs and the results on gas permeability are set out in Bouazza et al. (2006). The investigation was conducted on three sets of GCL samples which were prepared with different hydrating liquids. The first set of GCL samples was hydrated with deionised water (DI water), which formed a baseline test series. The second and third sets were hydrated with 0.0125 and 0.125 M calcium chloride (CaCl_2) solutions, respectively. All three sets of GCL were subjected to multiple wetting and drying cycles before their properties (Atterberg limits and swelling are considered in this paper) were assessed. The study was focused on determination of the effects of cation exchange and wet–dry cycles on the behaviour of the GCL but once the test results were available it became clear that the results could not properly be interpreted without consideration of the degree of cation exchange that was achieved in the wet–dry cycles. Unfortunately for some of the tests the precise quantities of calcium chloride solution used were not measured and have had to be estimated. It is hoped that publication of the methodology developed for the assessment of the degree of cation exchange will allow future researchers to ensure that more complete information is gathered during their tests.

2. Materials and methods

2.1. GCL

The GCL used in this study consisted of an essentially air dry, powdered sodium bentonite sandwiched between non-woven polypropylene geotextile layers. The geotextile layers were held together as a composite material by

needle punching. The cover and carrier geotextiles had reference masses per unit area of 0.27 and 0.38 kg/m², respectively. The initial thickness of the GCL (as received from the manufacturer) ranged from 7.6 to 8.9 mm and the average initial moisture content of the bentonite was 11% by dry mass. The mass per unit area of the oven-dry bentonite in the GCL ranged from 3.1 to 3.8 kg/m² with an average value of 3.34 kg/m² which was used for the analysis of the swell test data, etc. (note that this corresponds to an average of 3.7 kg/m² at the as-supplied 11% moisture content). The mineralogy of the bentonite in the GCL was investigated by X-ray diffraction (XRD) at an external commercial laboratory which reported that the clay contained 80% montmorillonite, 14% cristobalite, 4% quartz and 2% feldspar (Appendix A sets out an extract from the analytical report on the XRD). The cation exchange capacity of the bentonite was 90 milliequivalents (meq) per 100 g of dry clay.

2.2. Pore water

Calcium chloride was selected as a representative cation for the exchange tests as it is the predominant divalent cation observed in natural pore waters (Bohn et al., 1985; Lin and Benson, 2000). Based on the study by Lin and Benson (2000), a 0.0125 M calcium chloride solution was selected as the hydrating liquid to represent the concentration of divalent cations in a natural topsoil cover. A higher concentration, 0.125 M calcium chloride solution (10 times higher), was used to amplify the level of cation exchange effects for comparison purposes. Deionised water was used as the reference solution. Egloffstein (2000) pointed out that calcium concentrations in soil pore water generally range from 0.001 to 0.004 M (40–160 mg/L Ca^{2+}). Higher calcium concentrations are unlikely to be present in typical natural soils unless there are particular circumstances. For example, relatively high calcium concentration can be found in soils containing gypsum, a slightly soluble soil mineral found in some natural soils. Gypsum is soluble in low-salinity water to the extent of 0.015 M (600 mg/L Ca^{2+}); it is more soluble in strongly saline waters which can be important in saline and arid environments. Therefore, the calcium concentration 0.0125 M (500 mg/L Ca^{2+}), as used by Lin and Benson (2000), was deemed acceptable to represent the relatively high end of calcium concentrations in the pore water of general soils. However, as will be shown later in the discussion of the experimental results, the degree of cation exchange is sensitive to the total quantity of ions available per unit mass of bentonite as well as the pore water concentration. In the field, the quantity of calcium may be effectively unlimited compared with the mass of bentonite in a GCL, as calcium can be drawn from a large volume of adjacent pore water or supplied by release from adjacent soil. Thus in the field, with a calcium-containing pore water, effectively full conversion of a sodium bentonite to the calcium form may occur as the calcium is supplied by and sodium removed by groundwater

advection and diffusion. In contrast, in the laboratory with a finite quantity of water as in a liquid limit (LL) or swell test the degree of conversion will depend not only on the concentration of the ions in the water but also on the quantity of water. This is discussed in more detail in the following sections.

2.3. Atterberg limits

Atterberg limit tests were conducted following the Australian standard test methods for Atterberg limits (AS, 1995). Bentonite specimens were retrieved from the GCL and were mixed with deionised water and 0.0125 and 0.125 M calcium chloride solutions. After the Atterberg limits were measured (note: all tests were repeated at least twice), the bentonite was left to air dry in the laboratory environment (at controlled temperature of $21 \pm 1^\circ\text{C}$) until the loss of moisture ceased. Each bentonite specimen was then re-wetted with the same concentration of liquid as used initially. The bentonite specimens were tested for up to five wet–dry cycles. It should be noted that the presence of dissolved salts in the pore water of the samples complicates the interpretation of the moisture content results and hence the liquid and plastic limit (PL) results. This aspect is discussed in Section 3.

2.4. Swell tests

The GCL swell tests were performed using an oedometer consolidation cell. The GCL specimen was cut to size and placed in the 75 mm diameter oedometer ring which was then assembled into the oedometer cell. A normal stress of 20 kPa (representing a typical 1 m of soil pressure in a cover system) was applied on the GCL sample and a dial gauge was then fitted so that the swell of the GCL specimen could be monitored. Once the cell was assembled, the normal stress applied and the dial gauge in place, the oedometer cell was filled with 500 ml of the hydrating liquid. To determine an appropriate duration for the swell tests, a swell test was conducted over 14 days with deionised water (Fig. 1). This showed that the GCL swelled rapidly in the first 24 h of the hydration period; thereafter the swell rate decreased dramatically until a limiting swell was achieved. A hydration time of 4 days was therefore adopted for the other swell tests and this was considered reasonable to achieve 90% of the full hydration under 20 kPa surcharge (see Bouazza and Vangpaisal, 2003; Vangpaisal and Bouazza, 2004).

A set of 4 GCL specimens was used for the swell tests. All four specimens were cut from the same GCL sheet to minimise physical variation between the specimens. The first sample was hydrated with deionised water for all wetting cycles. The second and third samples were hydrated with deionised water in the first wetting cycle then hydrated with the 0.0125 and 0.125 M calcium chloride solutions, respectively, for the following wetting

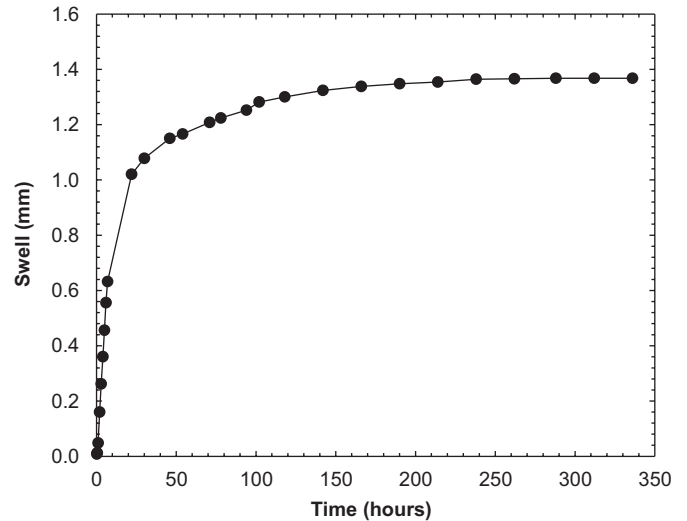


Fig. 1. Relation of GCL swell to hydration time under a 20 kPa surcharge.

cycles. The fourth sample was hydrated with the 0.0125 M calcium chloride solution for all wetting cycles. At the end of each hydration stage, the hydrating liquid was drained out and the excess liquid on the GCL surfaces was dabbed off. The GCL was then left to desiccate in the oedometer cell under the normal stress of 20 kPa for 15 days. A preliminary test showed that the GCL moisture content dropped to approximately 30–50% after 15 days of desiccation. To repeat the wet–dry cycle, the GCL was re-hydrated with the designated liquid and then re-desiccated following the same procedure.

3. Moisture content and change in mass of bentonite on cation exchange

Before considering the results of the various tests on the bentonite exposed to deionised water and the salt solutions, it is necessary to consider the effects of the salt solutions on the measured moisture content of the bentonite. It is also necessary to consider the degree of calcium exchange that is achieved for the bentonite and, as will be shown in the following sections, this varies significantly with the test conditions.

3.1. Moisture content measurement

The moisture content of the samples was measured by oven drying as is standard in soils work. However, the presence of dissolved salts in the pore water of the samples complicates the interpretation of the moisture content results. For example, consider a sample of clay with a saline pore water containing a mass, w_s , of dry soil grains. If the mass of pure water in the soil is w_w and dissolved in this water, there are salts at a total concentration of c grams of anhydrous salt per gram of pure water, then the actual moisture content (mass of pure water/mass clay) is given by $m_a = w_w/w_s$ but the moisture content measured by

a drying process, m_m will be given by

$$m_m = \frac{w_w - fw_w c}{w_s + w_w c + w_w c f} = \frac{w_w(1 - fc)}{w_s + w_w c(1 + f)}, \quad (1)$$

where $c(1 + f)$ is the mass of solids that would be recovered by evaporating a quantity of pore solution containing 1 g of pure water at the temperature of the moisture content test. The parameter f is required because some water of crystallisation may be held by the salts at the drying temperature. For example, calcium chloride can form hydrates with 1, 2, 4 and 6 moles of water of crystallisation per mole of the salt. This water is lost progressively on heating but it is possible that the hydrate with one mole of water of crystallisation is still stable at around 100 °C. However, as the moisture contents were determined at the standard temperature of 105 °C, it is unlikely that the calcium chloride will have retained any water of crystallisation in the moisture content test. Therefore, for the calculations set out below it has been assumed that the calcium chloride loses all water of crystallisation in the test (i.e. $f = 0$).

In addition to the actual and measured moisture contents, it is also useful to consider the volume of liquid in the soil as the volume of liquid will control physical effects—the salt ions occupy some volume in the solution and thus in a saline soil, the volume of liquid is greater than the volume of pure water in a soil containing the same mass of water. Of course there also will be chemical effects if the liquid contains salts which interact with the soil as in the present case. Thus a moisture content can be developed which represents that of a soil containing the equivalent volume of pure water to the volume of salt solution in the saline soil, that is a moisture content based on the mass of the equivalent volume of pure water per gram of clay. The ‘equivalent liquid volume’ moisture content, m_e is given by

$$m_e = \frac{w_w \rho_w (1 + c)}{\rho_{sn} w_s}, \quad (2)$$

where ρ_{sn} is the density of the pore solution and ρ_w is the density of water. *Note:* m_e is not the volumetric moisture content which is based on a volume ratio. Now, the density of a salt solution can be approximated by the formula:

$$\rho_{sn} \approx \frac{(1 + c)}{(1/\rho_w) + (c/\rho_{sa})}, \quad (3)$$

where ρ_{sa} is the effective density of the salts when in the solution, hence:

$$m_e \approx m_a \left(1 + c \frac{\rho_w}{\rho_{sa}} \right). \quad (4)$$

Analysis of density data for calcium chloride solutions shows that ρ_{sa}/ρ_w may be about 3.8 and thus for solutions where the concentration c is less than about 0.38 g calcium chloride per gram of water (380 g/L of water, a solution concentration of over 3 M) the ‘equivalent volume’ moisture content, m_e in ml/g, is numerically within 10%

of the actual moisture content m_a (i.e. $m_e \approx m_a$) and thus, m_a the actual moisture content allowing for the salt content may give a better indication of the behaviour of a soil than a measured moisture content which ignores the presence of the salt (at a salt concentration of 380 g/L for an actual moisture content of for example 30%, the measured moisture content would be 17%—a much greater error and one which increases with the value of the actual moisture content).

In this paper moisture contents are expressed either as measured moisture, m_m , content or actual moisture contents, m_a .

3.2. Change in mass of bentonite on cation exchange

In addition to the effect of the salts on the measured moisture content of the bentonite, there is a small effect of the exchange of calcium ions for sodium on the mass of bentonite particles. The exchange produces a small change in the dry mass of the bentonite and an inverse change in the mass of ions in solution. For example, if the bentonite has a cation exchange capacity of 90 meq/100 g dry clay then 1 g of dry bentonite will have 0.9 meq of associated sodium ions or $0.9 \times 23 = 20.7$ mg of sodium (the equivalent weight of sodium is 23). If the sodium is fully exchanged for calcium then 0.9 meq of calcium with a mass of $0.9 \times 20 = 18$ mg (the equivalent weight of calcium is 20) will replace the sodium and thus the mass of bentonite will drop by $(20.7 - 18) = 2.7$ mg/g of original clay. This represents an overall change of mass of -0.27% . As the change is small, it has been ignored in calculations presented in this paper and thus strictly all parameters expressed by mass of clay (bentonite) relate to the original mass of dry bentonite prior to exchange reactions. As the change in mass of ions sorbed on the bentonite is small, the corresponding change of the combined sodium plus calcium ion mass in solution also will be small and again has been ignored.

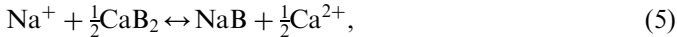
3.3. Ion exchange of calcium for sodium on the bentonite

For each of the test procedures, a sample of the bentonite or bentonite/geotextile system was exposed to calcium chloride solution and then allowed to dry. In the swelling tests, the GCL was immersed in calcium chloride solution so that ion exchange could occur between bentonite and the immersion fluid. In particular, water and calcium could enter the bentonite from the fluid and sodium could be lost to the fluid—that is the GCL sample was ‘open’ with respect to sodium, calcium and water all of which could be lost when the hydration liquid was drained out. In the Atterberg limit tests, calcium chloride solution was added to the bentonite, increasing the amount of water, calcium and chloride ions in the solution but the total amount of sodium in the system remained constant as water but not ions can be lost by drying—that is the system was closed with respect to sodium. The addition of calcium

will promote the conversion of sodium bentonite to the calcium form. However, for many of the tests insufficient calcium was added to fully convert the bentonite to the calcium form and this has important implications for the interpretation of the test results. To interpret the results of the various tests, it is necessary to know how the degree of exchange changes at each cycle of each test procedure recognising that the degree of exchange will depend on:

- the amount of calcium added (from the calcium chloride solution);
- the amount of sodium and calcium in the clay water system at any time (this depends on the experimental procedure—for example, is sodium progressively removed by replacing the solution in which a sample is immersed, or does the sodium remain as occurs in air or oven drying);
- the concentration of ions in the solution to which the bentonite is exposed (it will be shown that because monovalent sodium is being replaced by divalent calcium there is a concentration dependence).

The first step in analysing the fraction of sodium that is exchanged is to consider the exchange reaction. The sodium–calcium exchange for a bentonite can be represented by the equation:



where B represents moles of bentonite. Eq. (5) conforms to the Gaines Thomas convention (Gaines and Thomas, 1953 cited in Appelo and Postma, 1996). *Note:* there are other conventions, for example, the Gapon and Vanselow conventions. Appelo and Postma state that the choice of convention is largely a personal choice for the user but will depend on the availability of supporting data. From Eq. (5) and the law of mass action (see for example, Moore, 1962), at equilibrium the exchange position is given by

$$K_{\text{Na/Ca}} = \frac{[\text{NaB}][\text{Ca}^{2+}]^{0.5}}{[\text{CaB}_2]^{0.5}[\text{Na}^+]}, \quad (6)$$

where $K_{\text{Na/Ca}}$ is the selectivity coefficient of sodium bentonite for calcium and [Na] and [Ca] represent the activities of the sodium and calcium ions in the pore solution. For dilute solutions it may be assumed that

$$\begin{aligned} [\text{NaB}] &= \beta_{\text{Na}} \\ &= \frac{\text{Milliequivalents of sodium on the clay per 100 g clay}}{\text{Cation exchange capacity of the clay in milliequivalents per 100 g clay}} \end{aligned} \quad (9)$$

activities are equal to molalities. However, analysis of the data shows that in this work the solutions generally are not sufficiently dilute for this assumption to be valid (especially for samples in which ionic concentrations have been increased by drying).

3.4. The activity of dissolved ions in the clay pore water

For an ion, i , in solution in water at molality, m_i , the activity of the ion can be written as

$$\text{Activity} = \gamma_i m_i, \quad (7)$$

where the molality m_i is the number of moles of ion i per kg of water. There is a substantial literature on the assessment of activity coefficients, γ_i in solutions of different ionic strengths and a number of models are available (see for example, Nordstrom and Munoz, 1994). As solution concentrations become more concentrated, progressively more complex models are required to make allowance for ionic interactions and this requires consideration of the ionic strength of the solution.

Analysis of the solution data shows that the ionic strength of the clay pore water in this research was in the range 0.01–12. Nordstrom and Munoz (1994) state that for calcium chloride solutions up to an ionic strength of about 6, the Truesdell–Jones model for activity coefficients gives a good fit to the experimental data. This model therefore has been used in this paper for ionic strengths up to 6. For those solutions where the ionic strength is greater than 6, activity coefficients have been determined using the Phrqpitz computer code (Plummer and Parkhurst, 1990). The assessment of activity coefficients is discussed in more detail in Appendix B.

If allowance is made for the activity of the dissolved ions, Eq. (6) can be re-written as

$$K_{\text{Na/Ca}} = \frac{[\text{NaB}] \gamma_{\text{Ca}}^{0.5} m_{\text{Ca}}^{0.5}}{[\text{CaB}_2]^{0.5} \gamma_{\text{Na}} m_{\text{Na}}}, \quad (8)$$

where m_{Na} and γ_{Na} and m_{Ca} and γ_{Ca} are respectively the molality and activity coefficient of the sodium and the calcium ions in the solution.

3.5. Activity of ions sorbed onto the bentonite

To complete the analysis of the parameters in Eq. (8), it is necessary to consider the activity of the ions sorbed onto the solid bentonite minerals, i.e. [NaB] and [CaB₂]. These activities can be represented in a number of ways and the following analysis again conforms to the Gaines–Thomas convention (see Appelo and Postma, 1996 for fuller details) in which, the equivalent fraction of the exchangeable cations is used for the activity of the sorbed ions, thus:

Eq. (8) therefore becomes:

$$K_{\text{Na/Ca}} = \frac{\beta_{\text{Na}} \gamma_{\text{Ca}}^{0.5} m_{\text{Ca}}^{0.5}}{\beta_{\text{Ca}}^{0.5} \gamma_{\text{Na}} m_{\text{Na}}} \quad (10)$$

and if the bentonite is assumed to have been initially a pure sodium bentonite so that only sodium–calcium exchange need be considered then:

$$\beta_{Ca} = 1 - \beta_{Na} \tag{11}$$

and thus Eq. (10) can be solved for the β_{Ca} if the solution molalities and ion activities are known.

In principle, the activity of the ions on the solid clay could be further refined to take account of solution concentrations, etc. by the application of activity coefficients but Appelo and Postma (1996) note that data are not available on activity coefficients for solid phase exchange. However, they do provide information on the value of $K_{Na/Ca}$, the selectivity coefficient of sodium bentonite for calcium which they state “is around 0.4” and they suggest a range of 0.3–0.6. Whilst it might seem that to estimate the degree of exchange, it would be necessary to know the value of the selectivity coefficient more precisely. In practice, when calculating the percentage of sodium and calcium on a clay using Eq. (10) it was found that for the test conditions the value of β_{Ca} was relatively insensitive to the chosen value of the selectivity coefficient (see Fig. 2b which shows the estimated percentage of sodium on the clay for selectivity coefficients in the range 0.3–0.6—it can be seen that the effect of change of the coefficient is modest).

3.6. Effect of solution concentration on calcium–sodium exchange

Eq. (12), a rearrangement of Eq. (10), allows consideration of the effect of addition or removal of water from a system containing a fixed amount of sodium and calcium (e.g. concentration of the system by evaporation or dilution by the addition of pure water). For a system containing a fixed amount of sodium and calcium but a variable amount of water, it can be seen, from Eq. (12), that if $K_{Na/Ca}$ is effectively constant and if the ratio of activities changes only modestly with concentration then at low solution concentrations the square root relationship for the molality of calcium ion, m_{Ca} means that $[CaB_2]$ is preferred over $[NaB]$

$$\frac{[CaB_2]^{0.5}}{[NaB]} = \frac{\gamma_{Ca}^{0.5} m_{Ca}^{0.5}}{K_{Na/Ca} \gamma_{Na} m_{Na}^{0.5}} \tag{12}$$

However, if the overall solution concentration is increased, for example by drying, but without changing the total amounts of sodium and calcium in the clay–water system then the equilibrium will move in favour of $[NaB]$.

It may be noted that if the drying is sufficiently severe as to precipitate both sodium and calcium chlorides from the pore solution (as will occur in oven drying for example), then the final ion exchange state of the clay as it approaches dryness will be influenced by the relative solubilities of sodium and calcium chlorides at the drying temperature. Lide and Frederikse (1994) give the solubilities of sodium and calcium chlorides at 100 °C as 391 and

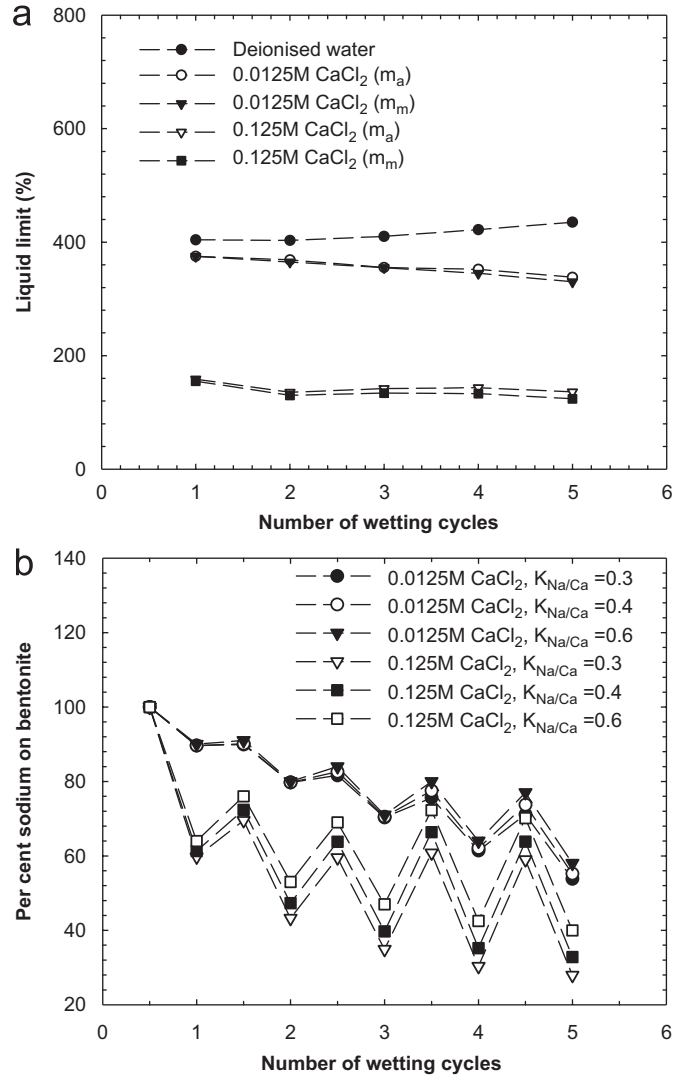


Fig. 2. (a) Liquid limit of bentonite from GCL (m_a = actual moisture content, m_m = measured moisture content) and (b) percent sodium on bentonite related to the number of wetting cycles and effect of selectivity coefficients.

1590 g/L, respectively. These figures correspond to molar concentrations of 6.7 and 14.3 moles/L, concentrations which may lead to a very different position for cation exchange equilibrium to that prior to drying (always provided that there is sufficient mass of calcium and sodium ion in relation to the mass of clay to influence the position of the ion exchange equilibrium). This demonstrates the considerable complexity in predicting the exchange behaviour of clays when wetting, drying and re-wetting are involved as, for example, the swell on re-wetting may be influenced by the state of cation exchange at the end of the previous drying cycle.

The quantity of calcium ion available will be an important consideration for the results reported in this paper—especially for the tests with 0.0125 M calcium chloride where there was often insufficient calcium for full conversion of the initially sodium bentonite.

4. Atterberg limit tests—data analysis and conversion

Before considering the results of the Atterberg limit tests, it is necessary to estimate the actual moisture contents and the degree of conversion of the bentonite from the sodium form to the calcium form using the procedures set out in the above discussion.

4.1. Actual moisture content estimation

For the Atterberg limit tests, the calculations for the conversion of measured moisture contents to actual moisture contents (as defined in Section 3) are set out in Table 1. For the calculations in this table, it was assumed that the initial moisture content of the bentonite prior to any addition of calcium chloride solution was 11% (the average value for the bentonite in the GCL as received). It was further assumed that for each wetting cycle a sufficient amount of the wetting solution was added to increase the measured moisture content of the bentonite to 10% above the measured LL and that, after the LL determination, the bentonite was allowed to dry to a measured moisture content of 15%. The choice of the figures, 10% and 15% was based on typical laboratory data but, as will be discussed later, the actual value used within a realistic range has rather little impact on the results of the calculations. The results shown in Table 1 are for 1 g of oven-dry bentonite powder from the GCL treated with the 0.0125 M calcium chloride.

The calculation procedure is as follows: for each LL determination, the mass of water added (column 4) is the amount of water necessary to bring the sample, from the previous air dry state to a measured moisture content equal to the new measured LL + 10% (the assumed maximum measured moisture content)—the measured LL being based on the original dry mass of bentonite plus the mass of dissolved calcium chloride added with the water as

discussed in Section 3.1. The procedure starts with a guessed value for the amount of this added water. The amount of salt that will be present in the dried bentonite is then calculated from the amount of salt that will have been associated with the water added. The measured maximum moisture content is calculated from the amount of water added and the total dry mass of the system (original dry mass of bentonite plus total calcium chloride added). The amount of water added is then refined iteratively until the calculated and measured moisture contents agree with an error of less than 0.1%.

Once the amount of calcium chloride in the system is known, the actual moisture content by mass of dry bentonite can be calculated. The final column, calcium added in meq, is calculated from the mass of calcium chloride added and is used in the next stage of the calculation—the estimation of the fraction of sodium remaining on the bentonite.

Using the procedure set out in Table 1, the measured liquid and PLs determined in the sequential wetting and drying tests were corrected to actual water contents per gram of initial dry bentonite and the results are as shown in Table 2. These results are considered below after assessment of the degree of calcium exchange achieved on the bentonite and the ionic strength of the pore liquid.

4.2. Fraction of sodium remaining on the bentonite after calcium chloride addition

The fraction of sodium on the bentonite was calculated at each stage of the wet–dry cycling of the Atterberg limit test programme. The results are set out in Tables 3a–d. For these calculations, the water in the system and the calcium added were calculated according to the procedure used to prepare Table 1. To calculate the fraction of sodium remaining on the clay, β_{Na} , a value was guessed and β_{Ca} calculated from Eq. (11). The sodium and calcium ion

Table 1
Conversion of measured liquid limit data to liquid limit data by actual moisture content for 0.0125 M calcium chloride additions

Measured liquid limit (%)	Assumed measured moisture content after air drying (%)	Assumed maximum measured moisture content, in liquid limit test (%)	Water added (g)	Calcium chloride added this cycle (mg)	Total mass of calcium chloride added (mg)	Mass clay plus added calcium chloride (g)	Liquid limit, actual water by initial mass of bentonite (%)	Calcium added to system per gram of original bentonite (meq)
375	11	385	3.76	5.22	5.22	1.005	377	0.09
365	15	375	3.64	5.05	10.27	1.010	369	0.19
350	15	360	3.50	4.86	15.13	1.015	355	0.27
345	15	355	3.47	4.81	19.94	1.020	352	0.36
330	15	340	3.33	4.62	24.57	1.025	338	0.44

Notes: The calculations are for 1 g of oven-dry bentonite and consider the measured liquid limit for four cycles of calcium chloride treatment and set out the estimated masses of calcium ion added at each cycle. The solution of concentration 0.0125 M (molar) used to add calcium to the clay, corresponds to 0.0125 moles of calcium chloride per litre of solution. When calculating the mass of calcium chloride added, it is necessary to know the mass of calcium chloride by mass of water, i.e. the molality of the solution. Using calcium chloride solution densities given in Perry (1963), a 0.0125 molar solution of calcium chloride has a molality (moles of salt per kg of water) of 0.01251. For the more concentrated solution the molality of 0.125 M corresponds to a molality of 0.1254 and thus in both cases the molarity and molality are sufficiently close to be used interchangeably.

Table 2
Summary of liquid and plastic limit data by measured and actual moisture contents

Measured liquid limit (%)	Liquid limit, actual water by initial mass of bentonite (%)	Measured plastic limit (%)	Plastic limit, actual water by initial mass of bentonite (%)
0.0125 M calcium chloride addition			
375	377	48	48
365	369	46	46
350	355	48	48
345	352	46	46
330	338	46	46
0.125 M calcium chloride addition			
155	158	47	47
130	135	44	45
134	142	45	46
133	143	45	46
124	136	45	46

Table 3a
Liquid limits and fraction of sodium on the bentonite (0.0125 M CaCl₂ solution)

Measured liquid limit (LL) and assumed air-dry moisture content (AD) (%)	Liquid limit, actual water by bentonite (%)	Water in system (ml/g clay)	Calcium added (meq)	Sodium in solution (meq/l)	Calcium in solution (meq/l)	Fraction of sodium on bentonite, β_{Na} (%)	$K_{Na/Ca}$
11 (AD)		0.11	0.000	0	0.00	100	0.400
375 (LL)	377	3.77	0.094	25	0.00	90	0.400
15 (AD)		0.15	0.094	597	27.00	90	0.400
365 (LL)	369	3.69	0.185	50	0.40	80	0.400
15 (AD)		0.15	0.185	1041	181	83	0.400
350 (LL)	355	3.55	0.273	75	1.60	71	0.400
15 (AD)		0.15	0.273	1338	4510	78	0.400
345 (LL)	352	3.52	0.359	97	4.60	62	0.400
15 (AD)		0.15	0.359	1558	790	74	0.400
330 (LL)	338	3.38	0.443	120	10.90	55	0.400

Note: AD = air dry.

Table 3b
Plastic limits and fraction of sodium on the bentonite (0.0125 M CaCl₂ solution)

Measured plastic limit (PL) and assumed air-dry moisture content (AD) (%)	Plastic limit, actual water by bentonite (%)	Water in system (ml/g clay)	Calcium added (meq)	Sodium in solution (meq/l)	Calcium in solution (meq/l)	Fraction of sodium on bentonite, β_{Na} (%)	$K_{Na/Ca}$
11 (AD)		0.11	0.000	0	0.00	100	0.400
48 (PL)	48	0.48	0.012	24	0.00	99	0.400
15 (AD)		0.15	0.012	78	0.04	99	0.400
46 (PL)	46	0.46	0.022	48	0.03	98	0.400
15 (AD)		0.15	0.022	146	0.30	98	0.400
48 (PL)	48	0.48	0.033	68	0.09	96	0.400
15 (AD)		0.15	0.033	217	0.90	96	0.400
46 (PL)	46	0.46	0.043	93	0.20	95	0.400
15 (AD)		0.15	0.043	284	2.10	95	0.400
46 (PL)	46	0.46	0.053	115	0.40	94	0.400

Table 3c
Liquid limits and fraction of sodium on the bentonite (0.125 M CaCl₂ solution)

Measured liquid limit (LL) and assumed air-dry moisture content (AD) (%)	Liquid limit, actual water by initial mass of bentonite (%)	Water in system (ml/g clay)	Calcium added (meq)	Sodium in solution (meq/l)	Calcium in solution (meq/l)	Fraction of sodium on bentonite, β_{Na} (%)	$K_{Na/Ca}$
11 (AD)		0.11	0.000	0.00	0.00	100	
155 (LL)	158	1.58	0.395	221	28.2	61	0.400
15 (AD)		0.15	0.395	1634	945	72	0.400
130 (LL)	135	1.35	0.722	353	181	47	0.400
15 (AD)		0.16	0.722	2105	2523	64	0.400
134 (LL)	142	1.42	1.065	385	365	40	0.400
15 (AD)		0.16	1.065	1918	4788	67	0.400
133 (LL)	143	1.43	1.412	409	575	35	0.400
15 (AD)		0.16	1.412	2027	6704	64	0.400
124 (LL)	136	1.36	1.740	448	832	33	0.400

Table 3d
Plastic limits and fraction of sodium on the bentonite (0.125 M CaCl₂ solution)

Measured plastic limit (PL) and assumed air-dry moisture content (AD) (%)	Plastic limit, actual water by initial mass of bentonite (%)	Water in system (ml/g clay)	Calcium added (meq)	Sodium in solution (meq/l)	Calcium in solution (meq/l)	Fraction of sodium on bentonite, β_{Na} (%)	$K_{Na/Ca}$
11 (AD)		0.11	0.000	0	0.00	100	
47 (PL)	47	0.47	0.116	241	5.30	87	0.400
15 (AD)		0.15	0.116	720	50.8	88	0.400
44 (PL)	45	0.45	0.215	442	41.9	78	0.400
15 (AD)		0.15	0.215	1156	264	81	0.400
45 (PL)	46	0.46	0.318	574	120	71	0.400
15 (AD)		0.15	0.318	1461	621	75	0.400
45 (PL)	46	0.46	0.421	677	237	66	0.400
15 (AD)		0.15	0.421	1683	1058	72	0.400
45 (PL)	46	0.46	0.524	753	379	62	0.400

concentrations in the solution were calculated in meq/litre and converted to moles/litre and the results inserted into Eq. (6). The guessed value of β_{Na} was then adjusted iteratively to achieve a value of 0.4 for the selectivity coefficient, $K_{Na/Ca}$. In order to enable an investigation of the sensitivity of the results to the actual value of the selectivity coefficient, the process was repeated for $K_{Na/Ca} = 0.3$ and 0.6, the range of values proposed by Appelo and Postma (1996).

5. Results and discussion

5.1. Atterberg limits: liquid limits

In Table 2, the Atterberg limit test results, LLs and PLs for the two calcium chloride solution concentrations are presented for each of the wet–dry cycles. The Atterberg

limits are presented in terms of both measured and actual moisture contents. It can be seen that the difference between the measured and actual moisture contents is modest but not trivial for the LLs after several cycles of calcium chloride addition. However, for the PLs the differences are minimal because of the small amount of calcium chloride solution required to wet the bentonite to the PL. Strictly for both the liquid and PL tests the amount of the calcium chloride solutions added to the clay at each wetting cycle should have been measured so that the fraction of sodium remaining on the clay could have been estimated from more precise data than the assumed LL + 10% for wetting and air dry moisture content of 15% on drying, but the effect of these assumptions is small. For example, if the wetting was 25% above the LL rather than 10%, then the effect on the calculated actual moisture content for the 0.0125 M calcium chloride would be to

increase the value, after 5 cycles of wetting and drying, from 338% to 338.5% an effect much below the precision of the test. For the 0.125 M solution, the increase, again after 5 cycles would be from 136% to 137.4%, again a trivial effect.

Fig. 2a shows the LL data from Table 2 plotted as a function of the wetting cycle and the fraction of sodium on the bentonite. Whilst it is appreciated that LL data can show some scatter, it appears that the LL with deionised water shows a slight but steady upward trend with wetting cycle and the LL with 0.0125 M calcium chloride solution shows a comparable downward trend, both of these trends are as expected. For the bentonite mixed with deionised water, the increase in the LL with each wetting and drying cycle is as expected as each cycle increases not only the energy put into mixing the bentonite but also the time for which it is in contact with water. Mixing energy and time can increase the degree of dispersion of dry bentonites as was shown by Jefferis (1982) who studied the development of apparent viscosity and shear modulus of bentonite slurries prepared with different levels of mixing energy and at different hydration times.

The bentonite mixed with the lower concentration calcium chloride solution (0.0125 M) had slightly lower values of LL, decreasing with each wetting and drying cycle as the fraction of sodium on the bentonite declined as is shown in Fig. 2b. This figure shows the estimated percentage sodium on the bentonite as a function of the wet–dry cycle. The wet–dry cycle number is plotted along the x -axis of the figure and the y -axis shows the estimated percentage sodium on the clay. On the x -axis the markers at full cycle numbers, 1, 2, 3, 4 and 5 represent wetting stages and the intermediate markers represent drying stages. Thus in Fig. 2b the ‘0.5’ marker point represents the initial dry bentonite, the marker ‘1’ the first wetting with calcium chloride and ‘1.5’ the first air drying. It should be remembered that the degree of exchange has been estimated using the Gaines–Thomas convention. Other conventions may give somewhat different results and thus Fig. 2b should be taken as giving an indication of the progress of cation exchange rather than precise values. The important message from Fig. 2b and one that is independent of the convention used is that the degree of exchange can be quite limited and very different for different test procedures.

From Fig. 2a, it also can be seen that the bentonite mixed with the higher concentration calcium chloride solution (0.125 M) had a LL of about 150 which changed little with the wetting and drying cycles. Also from Fig. 2a it can be seen that, for the 0.125 M calcium chloride treated bentonite, the proportion of sodium on the bentonite was reduced to 60% within the first wetting cycle which is comparable to the fifth cycle of the 0.0125 M treated bentonite.

This is confirmed in Fig. 3 which shows the LLs plotted as a function of the estimated percentage of sodium on the exchange sites of the bentonite. It can be seen that the

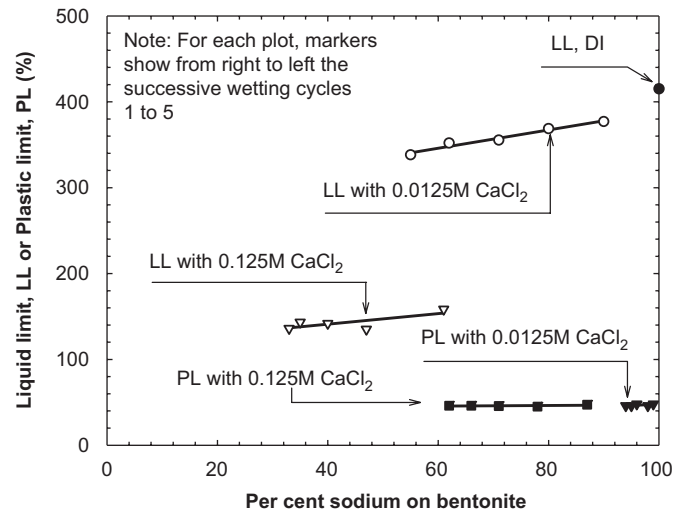


Fig. 3. Liquid and plastic limits, by actual moisture content, as a function of estimated fraction of sodium on the bentonite.

estimated percentages sodium for the last two wetting cycles with 0.0125 M calcium chloride overlap with the first cycle with the 0.125 M calcium chloride range—that is the percentage sodium for cycles 4 and 5 with 0.0125 M calcium chloride at 62% to 54% sodium overlaps with the first cycle with 0.125 M calcium chloride at 60% (note that the markers on the graph show the wetting cycles and that the cycles plot from right to left, i.e. the rightmost point is the first of the cycles). Despite the overlap of the percentage sodium (and thus the degree of calcium for sodium exchange), the LLs are very different for the 0.125 and 0.125 M treated bentonites. This difference in the results confirms that the LL is a function of the ionic strength of the pore fluid as well as the degree of cation exchange. Interestingly, the PL for the bentonite was relatively insensitive to both percentage sodium on the bentonite and the ionic strength of the two pore fluids—though note that, as the PL is significantly lower than the LL, the amount of fluid added to reach the PL was less than that to reach the LL and thus the degree of ion exchange achieved was less (a minimum of 60% sodium remained on the bentonite). At greater degrees of exchange and thus lower percentages of sodium, more effect might be expected but see the discussion in relation to the work of Williams et al. (1953).

The behaviour of clays is, in general, sensitive to the ionic strength of the pore fluid (see Eq. (10)) as well as the exchangeable ions associated with the clay and Stumm and Morgan (1996) show that an indicative double layer thickness ($1/k$) in nanometres for ions near a charged surface is given by

$$1/k = 0.304/\sqrt{I}, \quad (13)$$

where I is the ionic strength.

Fig. 4 shows the LLs and PLs plotted as a function of this indicative double layer thickness. It can be seen that whilst ionic strength is important, it alone cannot explain

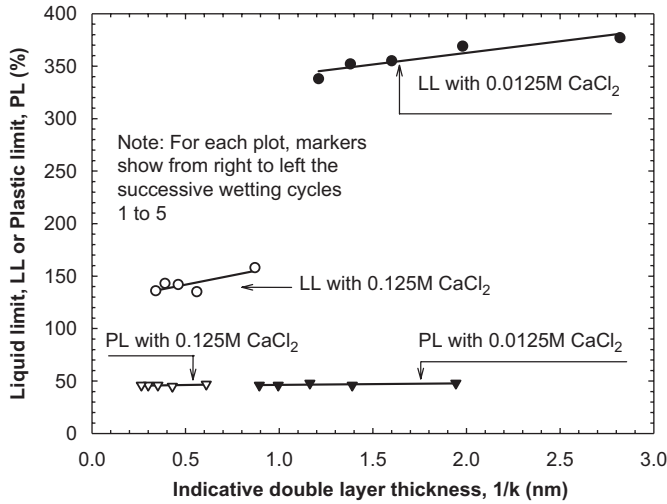


Fig. 4. Liquid and plastic limits as a function of indicative double layer thickness.

the difference between the LLs at the two calcium chloride solution concentrations. It is the combined effect of ionic strength and calcium exchange that is important at least for the two solution concentrations of 0.0125 and 0.125 M.

5.2. Atterberg limits: plastic limits

The PLs for the bentonite are tabulated in Tables 3c and d and shown in Fig. 5. It can be seen that although the PL of the sample wetted with deionised water, is slightly higher than that for the bentonite wetted with either of the calcium chloride solutions, the difference between the results for the three liquids is minimal. Consideration of Fig. 5 shows why the PL for the bentonite wetted with 0.0125 M calcium chloride is very similar to that for the deionised water. Minimal cation exchange of calcium for sodium has occurred since the PL (around 45%) is only modestly above the air dry moisture content and so little calcium chloride solution has been added and little cation exchange has occurred—by the fifth wetting cycle the proportion of sodium has been reduced only to 94%. Also the ionic strength of the pore water is possibly quite close to that of the pore water in the bentonite deionised water mix (when deionised water is added to bentonite some sodium ion will dissociate into the water).

Grim (1962) quotes values of the PL of calcium montmorillonites in the range 63–79% and sodium clays in the range 86–97%. He also quotes work by Williams et al. (1953) which suggests that for mixed sodium–calcium montmorillonites the highest value (higher than the value for either the pure calcium or sodium form) of PL may occur “at some particular ratio of calcium to sodium, such as 40:60”. It is therefore perhaps not surprising that the present experimental results with 0.125 M calcium chloride, which are for pure sodium bentonite and mixed calcium:-sodium bentonites, show little change with calcium chloride addition. By the fifth cycle with 0.125 M calcium

chloride, the percentage of sodium is reduced to 60% a value which according to Williams et al. (1953) may be near that which should give the maximum PL. However, with this predicted increase in PL with the increase in calcium percentage on the bentonite being offset by the increasing ionic strength of the pore liquid.

5.3. Swell tests

The results of the GCL swell tests are set out in Table 4 and Figs. 6 and 7. The GCL swell related to the number of wet–dry cycles for each of the hydrating liquids is shown in Fig. 6. The GCLs hydrated with deionised water and the two calcium chloride solutions are denoted as “DI”, “0.0125 M” “0.125 M”. The GCLs pre-hydrated with deionised water in the first cycle and then hydrated with calcium chloride solutions for the following cycles are denoted as “DI + 0.0125 M” and “DI + 0.125 M” as appropriate.

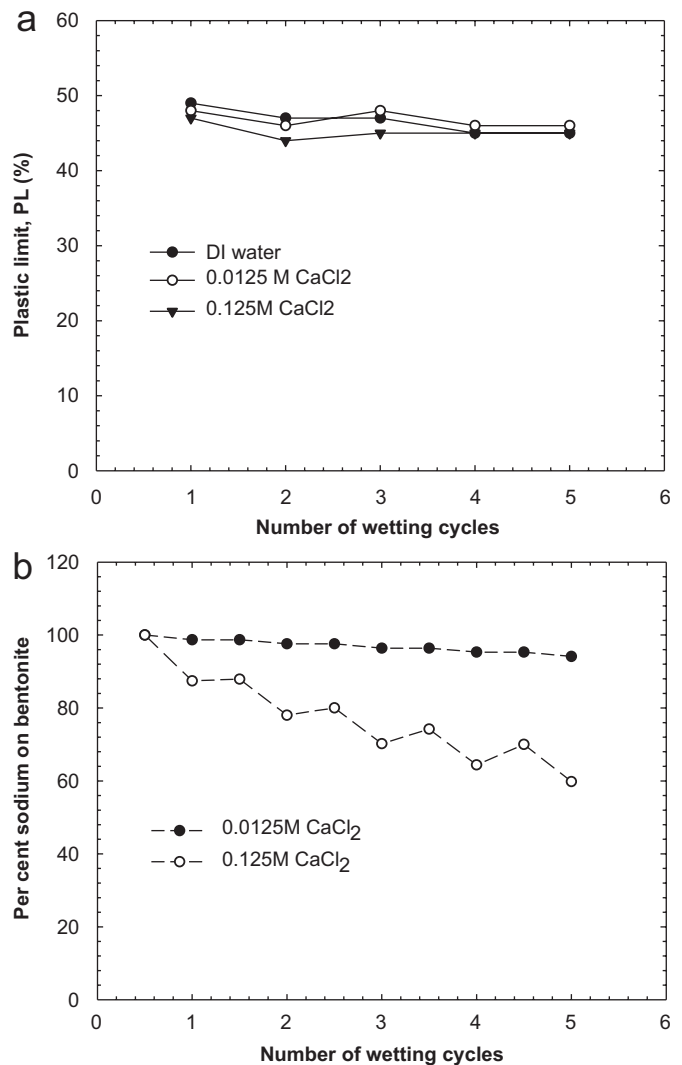


Fig. 5. (a) Plastic limit of bentonite from GCL and (b) percent sodium on bentonite, related to the number of the wetting cycle.

Table 4
Fraction of sodium on bentonite and measured swell under 20 kPa pressure

Immersion	Fraction of sodium on bentonite (%)		Swell (mm)		
	0.0125 M CaCl ₂ solution	0.125 M CaCl ₂ solution	Deionised water	0.0125 M CaCl ₂ solution	0.125 M CaCl ₂ solution
1	100	100	1.550	1.474 ^a	1.506 ^a
2	22.4	3.9	1.442	1.342	0.446
3	2.7	0.15	1.566	1.342	0.550
4	0.3	0.01	1.696	1.274	0.500
5	0.03	<0.01	1.700	1.176	0.482
6	<0.01	<0.01	1.552	0.822	0.420
7	<0.01	<0.01	1.584	0.816	0.438

^aThe first wetting of these samples was with deionised water, so these results are for swelling in DI water. The fraction of sodium on the sample first wetted with 0.0125 M CaCl₂ solution (see Figs. 6 and 7) will be as for the sample first wetted with DI water but shifted forward one immersion cycle.

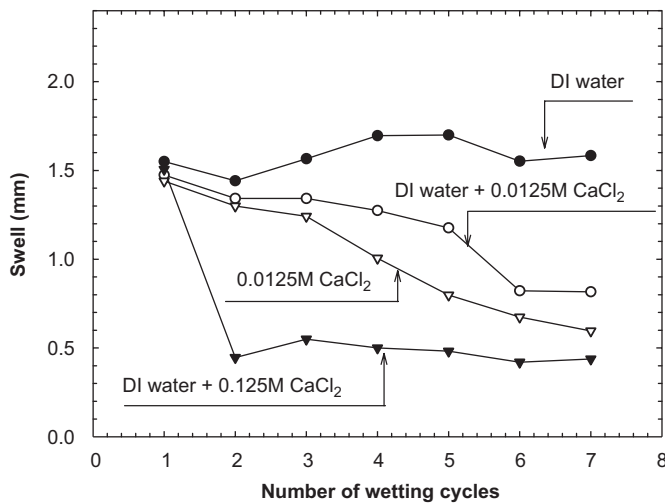


Fig. 6. Relation of GCL swell to the number of wetting cycles.

For the first wetting cycle, the amount of swelling for all four specimens was at the same level of about 1.5 mm. For the GCL hydrated with deionised water, the swelling was relatively constant throughout the seven wetting and drying cycles and an average swelling of 1.6 mm was recorded. This swelling is comparable to the extended swell test result presented in Fig. 1 (this was for 14 days rather than the 4 days used for the other tests and in common with the other swell tests was with a confining stress of 20 kPa). It should be noted that if the 1.6 mm swell is considered to be solely due to the intake of water into the bentonite and the initial air dry bentonite had a moisture content of 11% then the addition of water to a swell of 1.6 mm would increase the moisture content to just 57% which is relatively low—a bentonite could be expected to swell towards its LL if not subject to a significant confining stress (Jefferis and Jones, 2003). It therefore seems that a significant proportion of the bentonite swell under the 20 kPa applied load was taken up by bentonite penetration into the geotextile fabric.

The estimated fraction of sodium on the bentonite after each immersion cycle in the calcium chloride solutions is shown in Table 4 (note cycle 1 in this table is the first cycle in deionised water). The volume of calcium chloride

solution added to the swell test oedometer was 500 ml and the sample diameter was 75 mm giving a mass of dry bentonite in the cell of 15.2 g and a volume of liquid to dry bentonite ratio of 33 ml/g—much higher than in the liquid and PL tests. Furthermore, after each swell cycle the wetting liquid was disposed and replaced by a fresh batch of calcium chloride solution. Thus, sodium displaced from the bentonite, into the surrounding liquid, during each cycle was removed from the system. The overall result was that much higher degrees of calcium exchange were achieved in the swell tests than in the Atterberg limit tests as can be seen by comparing Tables 3a–d and 4. (Note: as the amount of liquid in the oedometer sample was large compared with the water retained in the sample at the end of a swell test, no allowance was made for this retained water and its associated salts when calculating the fraction of sodium remaining on the bentonite as shown in Table 4.) The same calculation procedure was used as for the Atterberg limit test results (i.e. the Gaines–Thomas convention was followed). It was assumed that there was sufficient time for chemical equilibrium, between the solution and the GCL sample in the oedometer, to be achieved by diffusion as the sample was relatively thin. However, this assumption may not have been valid—see the discussion below.

The swelling decreased when the GCL was in contact with 0.0125 M calcium chloride solution and the amount of swelling continued to decrease as the number of wet–dry cycles increased. The least amount of swell about 0.5 mm was recorded when the GCL was first exposed to a high-concentration solution (0.125 M CaCl₂) and only slight reduction in the GCL swelling was observed for the subsequent wet–dry cycles with this solution.

It can be seen from Table 4 that for the 0.0125 M calcium chloride solution the swell continued slightly to reduce even after the calculated fraction of sodium on the bentonite had reached near zero (i.e. full calcium exchange). However, in these tests the effect cannot have been due to a build-up in ionic strength of the wetting liquid (0.0125 M) as these were replaced at each cycle and therefore the ionic strength will have increased only to a very slight extent each cycle (due to liquid retained in the sample at the end of each swell test

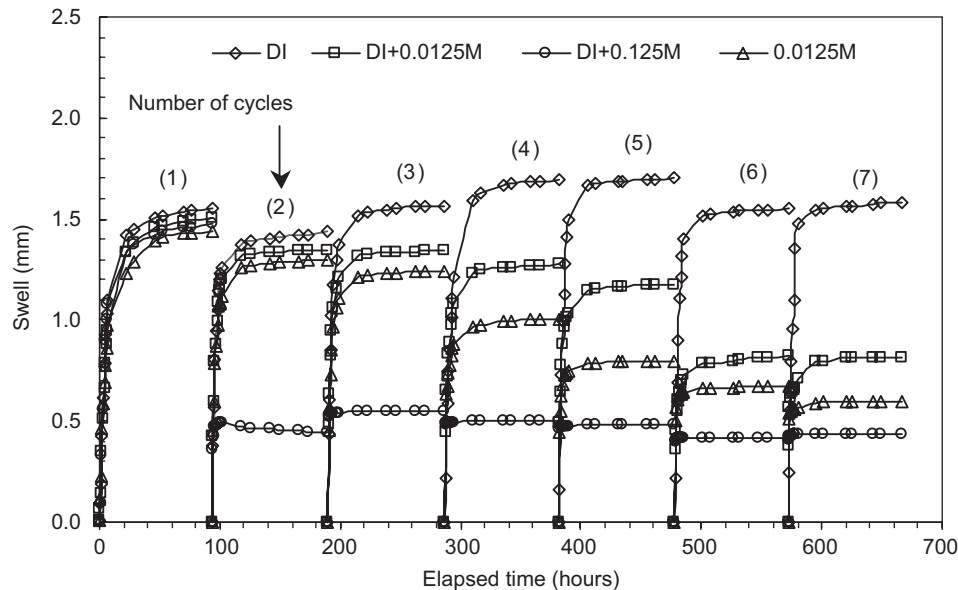


Fig. 7. Swell kinetic of GCL hydrated with different types of liquids for seven wetting cycles.

and the fact that some water was then lost during the air drying step). A possible explanation for the continuing decrease in swell independent of the calculated fraction of sodium on the bentonite is that equilibrium was not achieved in the oedometer sample between the GCL and the surrounding liquid. The sample was thin and an estimate based on simple diffusion theory suggests that equilibrium could have been achieved if there was no mass transfer. However, the requirement for mass transfer (sodium–calcium exchange) means that equilibrium will have been significantly retarded. In future cyclical tests involving cation exchange it may be useful to leave the GCL in contact with the liquid for much longer—or investigate the effects of immersion time. It is concluded that the time to achieve full swell without cation exchange may be a poor indicator of the time to complete swelling with cation exchange.

There is also a more subtle effect that can occur with thicker bentonite masses. As the liquid penetrates the bentonite, cation exchange will occur so that at the front of the penetrating solution calcium will be progressively depleted and exchanged for sodium. Thus, bentonite in the interior of a sample may be hydrated by a predominantly sodium chloride solution despite the fact that the surrounding solution is calcium chloride. Sodium chloride will have significantly less effect on swell as the ions are monovalent whereas the calcium ions are divalent. Of course exchange will continue, by diffusion, after the sample has been wetted until overall equilibrium is achieved but there will be little tendency for the swelled bentonite to shrink as the clay structure will have been opened up. For a thin sample, the effect may be limited as cation exchange is not instantaneous and there may be insufficient time for significant exchange to occur during the penetration of the wetting front.

Fig. 7 shows the swell of the GCL specimens for each wetting cycle as a function of time. It can be seen that calcium exchange gives a more rapidly swelling clay than the pure sodium bentonite. Indeed most of the swell was achieved within the first few hours of hydration. This is in line with water sorption data presented by Grim (1962) which showed that calcium bentonite took up water faster than sodium bentonite though the final amount of water sorbed was less.

In summary, the swell behaviour of the GCL is less limited than would be expected from the calculated degree of calcium exchange for each test liquid. This is possibly because full cation exchange equilibrium was not achieved between liquid and bentonite and was not achieved within the timescale of the swell test. In the field where timescales will be much longer, the effect on swell may be achieved in fewer cycles—though the limiting swell value, for matching chemical conditions may be unaffected as ultimately it is likely that near complete exchange, calcium for sodium, was achieved in the laboratory as is likely to occur in the field. Although the higher divalent cation concentration (0.125 M) is unlikely to occur in natural soils, continued permeation by a solution in which calcium ion dominates on a Gaines–Thomas basis (i.e. $[Ca^{2+}]^{0.5} > [Na^+]$ —as previously discussed, at low ionic strengths calcium is preferred because of the square root) will lead to full exchange of calcium for sodium—so reducing swell. It is clear that if in the field, a GCL is exposed to ions other than sodium, exchange will occur so changing the properties of the bentonite component. Therefore, the effect of wet–dry cycles coupled with cation exchange can be a major issue for consideration when a GCL is used in cover systems and not protected with a geomembrane—especially as drying in summer seasons may allow rapid inflow of calcium-containing water (calcium in equilibrium with

cover soil) on the next wetting. The effect of ionic strength of the pore fluid may be less significant in the field than in the laboratory as concentrations may be lower—though in dry seasons, as pore fluid is evaporated, concentrations may rise.

6. Conclusions

The cyclic wet–dry procedure has allowed detailed analysis of the effects of the degree of sodium–calcium exchange on the bentonite to be investigated and also has allowed consideration of the effects of ionic strength of the pore fluid. It is shown that for Atterberg limit tests, even using 0.125 M calcium chloride solution, full calcium exchange could not be achieved as there was insufficient calcium ion present in the quantity liquid necessary to bring the bentonite to the LL and this was particularly marked for the PL. For the swell tests which used a much higher liquid-to-solid ratios than was possible in the liquid and PL tests, full exchange could be achieved but only after several wet–dry cycles. The analysis of the degree of exchange achieved points out the need for careful consideration of the degree of exchange that actually is achieved when salts are added to bentonites in laboratory experiments. The degree of exchange may be much lower than many would have expected. Furthermore, the present paper shows how complex the analysis of exchange can become. It is suggested that researchers planning investigations of the effects of cation exchange processes should record the masses of solids and solutions used so that the liquid-to-clay ratios can be determined more precisely than was possible for the cation exchange data on which this paper was based. Also it will be important to undertake chemical analyses of the immersion fluids so that the calcium and sodium ion concentrations are known and degree of calcium–sodium (or other ion) exchange that has occurred can be quantified without having to invoke complex theoretical calculations which involve many assumptions. However, the analysis presented in this paper may provide a useful framework for anyone wishing to back-analyse papers in the substantial literature of the effects of cation exchange on the behaviour of bentonites where the degree of exchange achieved was not considered in the analysis of the results.

Finally, the cation exchange analysis shows that it can be difficult to reproduce field exchange conditions in the laboratory. In the field, the concentration of dissolved ions (e.g. calcium, magnesium, etc.) in a soil pore water may be relatively low due to mineral solubility controls. However, the mass of these ions in the soil may be very large compared with the ion total exchange capacity of the bentonite in a GCL. Furthermore, over time, the sodium may be lost from a GCL and the adjacent pore water by advection of groundwater and diffusion. As a result, the effective liquid/solid ratio in the field may be very large, much greater than in the laboratory tests (especially Atterberg limit tests). Thus despite low field concentra-

tions, full exchange may be achieved with less damaging effects than are found in the laboratory with strong calcium solutions where ionic strength has a damaging effect as well as the cation exchange.

Acknowledgements

This study was financially supported by a Discovery grant awarded to the first author by the Australian Research Council to investigate gas migration through GCLs. Sincere appreciation is extended to the Council. The GCL samples were donated by Soil Filters Pty. Ltd. and Geofabrics Australasia Pty. Ltd, their support is gratefully acknowledged.

The authors thank the anonymous reviewers who have contributed considerably to the development of this paper and for suggesting that the effects of ionic strength on activity should be considered. This has allowed a fuller theoretical model of the exchange process to be developed.

Appendix A. Mineralogical analyses of the bentonite from the GCL

The GCL bentonite component used in this investigation was mineralogically analysed by XRD. The analyses were performed by CSIRO Land and Water, Adelaide, Australia. Three XRD analyses were carried out with different sample preparation procedures. In the first procedure, the bentonite samples were ground in an agate mortar and pestle and pressed into aluminium sample holders for XRD analysis. For the second procedure, the bentonite samples from the first procedure were ground further in a micronising mill before being analysed. In the third procedure, the micronised bentonite samples were Ca saturated by CaCl_2 solution before analysed. XRD patterns were recorded with a Philips PW1800 microprocessor-controlled diffractometer using $\text{Cu K}\alpha$ radiation, variable divergence slit and graphite monochromator.

Quantitative analysis results are shown in Table A1. The values in parenthesis are the errors in the last significant figure reported from Siroquant, a commercial package used in the analyses. The results are normalised to 100%, and hence do not include unidentified or amorphous materials.

The bentonite sample was composed of mixtures of smectite (montmorillonite), cristobalite, quartz and feldspar (Ca albite).

Table A1
Mineralogical compositions of GCL bentonite component

Mineral	GCL-1
Smectite	80(2)
Cristobalite	14(1)
Quartz	4(1)
Ca albite	1(1)
Calcite	—
Hematite	—

Appendix B. Activity of ions in soil pore water

As stated in the main text, there is a substantial literature on the assessment of the activity of ions in solution. For dilute solutions relatively simple models may be appropriate but as solution concentrations increase progressively more complex models are required and the ionic strength of the solution becomes an important parameter.

The ionic strength, I of a solution containing ions i of molality m_i and charge z_i is given by (see for example Moore, 1962)

$$I = 0.5 \sum m_i z_i^2, \quad (\text{B.1})$$

Using the above formula, it can be shown that for the 0.0125 and 0.125 M solutions of calcium chloride, the ionic strengths are 0.0375 and 0.375 g/mole, respectively. Exchange of the calcium by sodium (as will occur on exposure to a sodium bentonite) will reduce the ionic strength of the solution as $z_{\text{Ca}} = +2$ whereas $z_{\text{Na}} = +1$ but noting that 2 moles of sodium will be released into solution from the bentonite for every mole of calcium taken up on the bentonite and thus $\delta m_{\text{Na}} = 2 \times \delta m_{\text{Ca}}$ where δm is the change in molality. If full exchange were to occur so that all the calcium in the calcium chloride solutions was replaced by sodium then the ionic strengths of the two solutions would be reduced to 0.025 and 0.25, respectively. It follows that for a closed clay–water system (one in which there is no exchange of ions or water with the outside environment), the ionic strength of the pore water associated with bentonite will vary with the degree of ion exchange.

Nordstrom and Munoz (1994) state that for solutions up to an ionic strength of about 6 ($I = 6$), the Truesdell–Jones approximation can be used to estimate the individual ion activities as follows:

$$\log_{10} \gamma_i = -z_i^2 \frac{A\sqrt{I}}{1 + Ba\sqrt{I}} + bI, \quad (\text{B.2})$$

where A and B are empirical parameters and a and b are ion activity coefficients. Langmuir (1997) gives a discussion on the derivation of Eq. (A2.2) and using his data and a temperature of 21 ± 1 °C (the laboratory temperature) A can be interpolated to be $0.5066 \pm 0.0008 \text{ mol}^{-1/2} \text{ kg}_{\text{H}_2\text{O}}^{1/2}$ and B to be $0.3278 \pm 0.0002 \text{ cm}^{-1} \text{ mol}^{-1/2} \text{ kg}_{\text{H}_2\text{O}}^{1/2}$ and thus for the laboratory temperature range, the values of A and B are effectively constant at 0.5066 and $0.3278 \text{ cm}^{-1} \text{ mol}^{-1/2} \text{ kg}_{\text{H}_2\text{O}}^{1/2}$, respectively. NB as noted A and B are empirical constants and different authors give slightly differing values.

Langmuir (1997) gives values for a and b , the individual ion activity coefficient parameters as follows:

Ion	a parameter	b parameter
Sodium	4.0	0.075
Calcium	5.0	0.165

For the solutions with ionic strength greater than 6, the phrqpitz code for geochemical calculations in brines

(Plummer and Parkhurst, 1990) was used to estimate activity coefficients. This is a code specifically adapted for brines (concentrated saline solutions) and uses the Pitzer virial-coefficient approach for activity coefficient corrections. Using the code, activity coefficients were estimated for a series of concentrated calcium and sodium chloride solutions and the ratio $(\gamma_{\text{Ca}})^{0.5}/\gamma_{\text{Na}}$, as required in Eq. (10), was calculated and the results then used in the iterative process required to develop Tables 3 and 4.

References

- Appelo, C.A.J., Postma, D., 1996. *Geochemistry and Groundwater Pollution*. Balkema, Rotterdam.
- Australian Standards, 1995. *Methods of testing soils for engineering purposes: soil classification tests*. AS1289.3.1.1/3.2.1.
- Barroso, M., Touze-Foltz, N., von Maubeuge, K., Pierson, P., 2006. Laboratory investigation of flow rate through composite liners consisting of a geomembrane, a GCL and a soil liner. *Geotextiles and Geomembranes* 24 (3), 139–155.
- Bohn, H., McNeal, B., O'Connor, G., 1985. *Soil Chemistry*. Wiley, New York.
- Bouazza, A., Vangpaisal, T., 2003. An apparatus to measure gas permeability of geosynthetic clay liners. *Geotextiles and Geomembranes* 21 (2), 85–101.
- Bouazza, A., Vangpaisal, T., 2006. Laboratory investigation of gas leakage rate through a GM/GCL composite liner due to a circular defect in the geomembrane. *Geotextiles and Geomembranes* 24 (2), 110–115.
- Bouazza, A., Vangpaisal, T., Jefferis, S., 2006. Effect of wet–dry cycles and cation exchange on gas permeability of geosynthetic clay liners. *Journal of Geotechnical and Geoenvironmental Engineering* 132 (8), 1011–1018.
- Dickinson, S., Brachman, R.W.I., 2006. Deformations of a geosynthetic clay liner beneath a geomembrane wrinkle and coarse gravel. *Geotextiles and Geomembranes* 24 (5), 285–298.
- Egloffstein, T.A., 2000. Natural bentonites-influence of the ion exchange and partial desiccation on permeability and self healing capacity of bentonites used in GCLs. In: *Proceedings Fourteenth Geosynthetic Research Institute Conference*, pp. 164–188.
- Egloffstein, T.A., 2001. The influence of ion-exchange on the permeability of geosynthetic clay liners (GCLs) in landfill capping systems. In: *Proceedings of the Eighth International Waste Management and Landfill Symposium*, Cagliari, pp. 207–218.
- Egloffstein, T.A., 2002. Bentonite as sealing material in geosynthetic clay liners-influence of the electrolyte concentration, the ion exchange and ion exchange with simultaneous partial desiccation on permeability. In: *Proceedings of the International Symposium on Clay Geosynthetic Barriers*, Nuremberg, pp. 141–153.
- Gaines, G.L., Thomas, H.C., 1953. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. *Journal of Chemical Physics* 21, 714–718.
- Grim, R.E., 1962. *Applied Clay Mineralogy*. McGraw Hill Book Company, New York.
- Hurst, P., Rowe, R.K., 2006. Average bonding peel strength of geosynthetic clay liners exposed to jet fuel A-1. *Geotextiles and Geomembranes* 24 (1), 58–63.
- James, A.N., Fullerton, D., Drake, R., 1997. Field performance of GCL under ion exchange conditions. *Journal of Geotechnical and Geoenvironmental Engineering* 123 (10), 897–901.
- Jefferis, S.A., 1982. Effects of mixing on bentonite slurries and grouts. *Grouting, Soil Improvement and Geosynthetics*, ASCE, Geotechnical Special Publication no. 30, pp. 1393–1402.
- Jefferis, S.A., Jones D.R.V., 2003. Hydraulic properties of geosynthetic clay liners. In: *Proceedings of the First National Geosynthetics*

- Symposium, Geosynthetics, Protecting the Environment, Nottingham, pp. 33–49.
- Langmuir, D., 1997. *Aqueous Environmental Geochemistry*. Prentice Hall, Englewood Cliffs, NJ.
- Lee, J.M., Shackelford, C.D., 2005. Impact of bentonite quality on hydraulic conductivity of geosynthetic clay liners. *Journal of Geotechnical and Geoenvironmental Engineering* 131 (1), 64–77.
- Lide, D.R., Frederikse, H.P.R., 1994. *CRC Handbook of Chemistry and Physics*, 75th ed. CRC Press, Boca Raton, FL.
- Lin, L.C., Benson, C.H., 2000. Effect of wet–dry cycling on swelling and hydraulic conductivity of GCLs. *Journal of Geotechnical and Geoenvironmental Engineering* 126 (1), 40–49.
- Mazzieri, F.P., Pasqualini, E., 2000. Permeability of damaged geosynthetic clay liners. *Geosynthetics International* 7 (2), 101–118.
- Melchior, S., 1997. In-situ studies on the performance of landfill caps. In: *Proceedings of the First International Conference on Containment Technology*, St. Petersburg, pp. 365–373.
- Melchior, S., 2002. Field studies and excavations of geosynthetic clay barriers in landfill covers. In: *Proceedings of the International Symposium on Clay Geosynthetic Barriers*, Nuremberg, pp. 321–330.
- Moore, W.J., 1962. *Physical Chemistry*, fourth ed. Longmans.
- Nordstrom, D.K., Munoz, J.L., 1994. *Geochemical Thermodynamics*, second ed. Blackwell Scientific Publications, Oxford.
- Perry, J.H., 1963. *Chemical Engineers' Handbook*, fourth ed. McGraw Hill Book Company, New York.
- Plummer, L.N., Parkhurst, D.L., 1990. Application of the Pitzer Equations to the PHREEQE geochemical model. *Chemical modeling of aqueous systems II: American Chemical Society Symposium Series* 416. American Chemical Society, Washington, DC, pp. 128–137.
- Southen, J.M., Rowe, R.K., 2005. Modeling of thermally induced desiccation of geosynthetic clay liners. *Geotextiles and Geomembranes* 23 (5), 425–442.
- Stumm, W., Morgan, J.L., 1996. *Aquatic Chemistry*. Wiley, New York.
- Touze-Foltz, N., Duquennoi, C., Gaget, E., 2006. Hydraulic and mechanical behaviour of GCLs in contact with leachate as part of a composite liner. *Geotextiles and Geomembranes* 24 (2), 188–197.
- Vangpaisal, T., Bouazza, A., 2004. Gas permeability of partially hydrated geosynthetic clay liners. *Journal of Geotechnical and Geoenvironmental Engineering* 130 (1), 93–102.
- Williams, F.J.M., Neznayko, M., Weintritt, D.J., 1953. The effects of exchangeable bases on the colloidal properties of bentonite. *Journal of Physical Chemistry* 57, 6–10.