## Using Neutron Spectroscopy to Measure Soil Water Retention at High Suction Values

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USING NEUTRON SPECTROSCOPY TO MEASURE SOIL WATER RETENTION AT HIGH SUCTION VALUES

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ABSTRACT

Laboratory determination of water retention curves for geosynthetic clay liners (GCLs) and their bentonite components are time-consuming, especially for high suction ranges. This paper explores the potential use of neutron spectroscopy as a useful method to assess the water retention properties of montmorillonite at suction levels >10 MPa for GCL studies. The results from neutron spectroscopy are in good agreement with traditional methods when assessing the water retention of bentonite and GCLs. Additionally, the primary advantage of neutron scattering is that, contrary to conventional methods, water populations within the clay matrix, such as bulk-like water, confined water and structure OH, are observed and can be quantified independently.

Keywords: Bentonite, water retention, high suction, geosynthetic clay liners

INTRODUCTION

Geosynthetic clay liners (GCLs) are engineered hydraulic barriers made of a thin (5-10 mm) layer of bentonite encased between two geotextiles which have become a ubiquitous feature in lining systems for waste containment facilities (Bouazza 2002). GCLs are commonly installed at low gravimetric water content (≈10%) on a subsoil and are covered by a geomembrane immediately after field installation. Thus, their hydration occurs through water transfer from the underlying soil, which is governed by the water retention curve (WRC) of the GCL. The WRC relationship is fundamental for estimating the ultimate degree of saturation attained by GCLs and the equilibrium times required for hydration/dehydration. In the high suction range (>10 MPa) the WRC is particularly crucial for assessing GCL behaviour, both in the
hydration (Bouazza et al. 2017a; Acikel et al. 2018a) and dehydration (Azad et al. 2011; Rowe and Verge 2013; Bouazza et al. 2017b) regimes, for example as pertains to conditions existing on exposed side slopes of landfills (Ashe et al. 2014; Rowe et al. 2016) or mining applications (Hornsey et al. 2010; Bouazza et al. 2013, 2014). Methods commonly used to explore high suction ranges in GCLs are the vapour equilibrium technique (VET) (Daniel et al. 1993; Rouf et al. 2016), capacitive relative humidity sensors and adaptations of the filter paper method (Abuel-Naga and Bouazza 2010; Beddoe et al. 2011; Acikel et al. 2015). These techniques are accurate and reliable, but a single WRC can require several weeks to be acquired, primarily due to the low permeability of the bentonite (the hydraulically active component of the GCL).

Inelastic neutron scattering (INS) is a spectroscopic technique that can be applied to obtain a WRC for a single sample during both dehydration and rehydration within a few days that has relevance to GCL behaviour at high suction. On the other hand, while traditional methods can only assess water content as a whole, INS (and in particular quasielastic neutron scattering, QENS) provides unique information about different water populations present in the clay, which can be advantageous when analysing the hydration conditions in GCLs and similar clay-based materials as it allows differentiating long range diffusive motions.

**Neutron scattering**

The measurement of momentum and energy transfer from matter by neutron scattering makes this technique a powerful tool to study clay-water interactions. The hydrogen (H) atom, as a component of water as well as part of the structure of montmorillonite (Mt; \( \text{Na}_{0.8}(\text{Si}_{0.77}\text{Al}_{0.23})(\text{Al}_{1.10}\text{Fe}_{0.30}\text{Mg}_{0.61}\text{O}_{20})(\text{OH}_4)\cdot n\text{H}_2\text{O} \); Gates et al. 2017), possesses a substantial incoherent scattering cross section compared to all other atoms (Kelman 2016), increasing the potential for preferentially observing H (as H\(_2\)O or OH herein) during INS experiments. Indeed, NS has been used to study the mobility of water in Mt over the last several decades (e.g. Olejnik et al. 1970; Adams et al. 1979; Cebula et al. 1981; Cases et al. 1992; Bérend et al. 1995; Saiyouri et al. 2000; Ferrage et al. 2005; Michot et al. 2007; Bordallo et al. 2008; Gonzalez Sanchez et al. 2008; Marry et al. 2011; Gates et al. 2012, 2017). For general descriptions of neutron scattering applied to clay minerals see the reviews by Dove (2002) and Martins et al. (2014).
Elastic and quasielastic neutron scattering

Figure 1 presents a simplified description of a typical quasielastic neutron scattering (QENS) spectrum. The elastic signal represents the contribution from protons seen as being immobile (structural hydroxyl, OH) as well as water that is slower than the observation time defined by the instrument resolution function (Lechner 2001). On the other hand, if water is moving faster than the observation window it is not seen in the quasielastic (QE) signal, but instead is incorporated into the background (Figure 1). The QE signal originates from energy exchange between the neutron and can be attributed to diffusive motions arising from the different water populations in the clay-water system. In broad terms, this QE signal response in clay minerals can be divided into confined water and different bulk-like water populations, in our example bulk-like water 1, bulk-like water 2 and confined water. The intensity and width of the QE response of the measured neutron scattering cross section, $S(Q,\omega)$, is influenced by the instrument resolution, the energy of the neutron beam and the type of motion that the protons are undergoing (Martins et al. 2014). A sample with more water will generally present an intense and broader QE signal (bulk-like water 1 + bulk-like water 2), whereas, a dryer sample will only present fewer population (in our example bulk-like water 1, and confined water, which means that the QE signal is less intense and narrower). Consequently, the line width of the QE signal provides a quantitative measure of gravimetric water content (GWC), as has been shown recently by Gates et al. (2017).

MATERIAL AND METHODS

GCL

The GCL examined consisted of powdered sodium bentonite (Queensland, Australia) contained between the nonwoven cover and scrim-reinforced carrier geotextiles, needle-punched together and thermally treated. The GCL physical characteristics are summarised in Table 1. The mass per unit area of bentonite ($M_b$) was calculated as the difference between the total mass per unit area of the GCL ($M_{GCL}$) and mass per unit area of the geotextiles ($M_{GTX}$). $M_{GCL}$ and $M_{GTX}$ were obtained as per ASTM D5993 and ASTM D5261-10, respectively. The
properties and mineralogical composition of the bentonite from the GCL are shown in Tables 2 and 3.

Sample preparation

Bentonite was removed from the GCL and the <0.2μm fraction was isolated and concentrated by sedimentation and centrifugation methods (Fehervari et al. 2016) to obtain a homionic Na⁺-montmorillonite (NaMt). The <0.2 μm fraction recovered by centrifugation is ≈53% (±3%) of bulk (Fehervari et al. 2016). After the purification procedure, the purified NaMt sample (=0.5g at oven-dried condition) was hydrated to form a 5% aqueous dispersion. Then, an annular aluminium sample holder insert was repeatedly dipped into the aqueous dispersion to deposit the sample onto the outer surface of the holder (Gates et al. 2017). Then, the sample holder was connected to a vacuum vapour exchange system to allow rapid (2 hr) water vapour exchange during the hydration/dehydration cycle of the experiment.

INS experiment procedure

Measurements were made at the direct time-of-flight spectrometer (PELICAN) located at the Australian Centre for Neutron Scattering, which is part of the Australian Nuclear Science and Technology Organization (ANSTO) facilities, Australia. A computer controlled vapour pressure delivery system provided a series of water vapour pressures (which can be expressed in % relative humidity, RH) to the sample environment at 22°C. The sequence used (in RH) was: 85, 75, 55, 35 and 0.4%, and then back to 85% using the same steps. During the sequence, the sample lost or absorbed water in reaction to the new RH condition imposed, and INS data were collected continuously for 4 hours in 20-minute blocks to evaluate when the equilibrium was achieved for each RH condition (see Gates et al. 2017). The experiment only took seven days to be finalised. Lastly, after the experiments were conducted, the samples were oven dried to obtain the dry mass and therefore calculate the gravimetric water content at each RH condition.

VET experiment procedure

VET tests were conducted on the same sample as used for the INS measurements following procedures given in Rouf et al. (2016) for GCL vapour phase hydration using super-saturated
salt solutions. The measurements were done subsequent to the INS experiments by removing the aluminium insert, onto which the sample was adhered, from the outer aluminium case and equilibrating it within a desiccator above the appropriate salt solutions. The salt solutions of KCl, NaCl, CH3COOK and LiBr imposed, respectively, RH conditions of 85, 75, 23 and 7% (ASTM E104). Hence, a similar sequence of dehydration/rehydration employed in the INS experiment was replicated using the VET at 22°C. The RH inside the vacuum desiccator was verified using an RH sensor to assure that the target RH was attained. The equilibrium mass of the sample was recorded after 5 to 6 days for each RH stage, thus requiring seven weeks for completion of the VET measurements.

RESULTS AND DISCUSSION

The total INS scattering cross section \( S(Q, ω) \) representing all protons in the sample was calculated over a broad (±2.0 meV) energy transfer range (Figure 1), whereas the elastic signal was calculated from a narrow (±0.8 meV) energy transfer range to represent protons that are largely immobile within the resolution window used in the experiment (wavelength \( λ = 5.97 \text{ Å} \); energy resolution = 65 µeV; time window = 63 ps). Since differences in the concentration of protons within each of these energy ranges are directly related to the sample hydration state, the amount of water in the sample can be precisely determined. To do so, the total, elastic and QE signals were determined, at each RH stage, by summing the scattering intensities within the appropriate transfer energy limits as described in Gates et al. (2017) using Eq. 1 below. The amount of proton within the narrow energy transfer range, i.e., the structural OH and water seen as immobile, both contributing to the elastic signal, were first normalized to the mass of the dry clay and to the elastic signal of the driest sample (RH = 0.4%). This latter step was necessary to account for residual water present in the driest sample. The QE signal representing all the mobile water in the sample was then obtained by subtraction of the elastic signal from the total signal over the course of the experiment:

\[
Total \text{ water} = \frac{Total \text{ signal} - (Elastic \text{ signal} (M(1 - OH))) \times (Elastic \text{ signal})_{Driest \text{ sample}}}{(Elastic \text{ signal})_{Driest \text{ sample}}}
\]

where \( M \) is the mass of dry clay (≈0.5g), \( OH \) is the fractional structural OH content (0.091g, Gates et al. 2017), and \( (Elastic \text{ signal})_{Driest \text{ sample}} \) is the elastic signal from the sample at RH=0.4%. Eq. 1 requires precise knowledge of the structural chemistry of the sample (Table

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3), simply because the signal within the ±0.8 meV integration limit contains contributions from protons associated with structural OH in the clay mineral as well as a small amount of water seen as immobile in the equipment resolution.

Figure 2 shows the resulting total, elastic and QE signals calculated at each RH stage by application of Eq. 1. The Kelvin equation (eq. 2) allows the RH values to be expressed in terms of suction potential, where $\Psi_t$ is the total suction (Pa), $R$ is the universal gas constant (8.31432 J/mol per K), $T$ is absolute temperature (K), $v$ is the specific volume of water (i.e. the reciprocal of specific mass, m$^3$/kg), $M$ is the molecular mass of water vapour (18.016 kg/kmol). Eq. 2 has been used for both measurement techniques, i.e., INS and VET, respectively.

$$\Psi_t = -\frac{RT}{vM\ln \left(\frac{RH\%}{100}\right)} \quad (2)$$

The results obtained from the INS (GWC in Eq. 1) and on the same sample by VET experiments are in good agreement (Figure 3). The INS data presented was directly calculated from Eq. 1, where the scaling factor is the normalisation for structural hydroxyl content, immobile water and sample mass. No other numerical manipulations were performed, and the INS error bars represent the average signal error (≈1.9 mg/g), which was done by iteratively adding and subtracting the error on the signal (returned by the instrument) to the average signal for each RH. The error bars for the VET were assessed as 10 mg/g. Thus INS is highly accurate compared with any traditional technique.

During dehydration, a log-linear decrease in GWC was observed in the VET results, whereas INS results showed a slight deviation from log-linearity at the 85% RH condition. The reason is that, during the rehydration path, equilibrium was not fully achieved within 4 hours. Water “leaves” (dehydrates) the interparticle spaces of the clay more efficiently than it “enters” (rehydrates) into the interparticle spaces. Thus pseudo-hysteresis occurs because higher energy is required to open the interlayer space between smectite layers and allow water to enter.

Comparison of INS results with GCL water retention data

The dehydration results from the INS and VET experiments were compared with previous studies conducted with GCL, from which the powder NaMt sample was taken for the current
investigation (Acikel 2016; Rouf et al. 2016; Bouazza et al. 2017a). To make the comparisons valid, two conversions were required: (a) conversion of GCL water content data into bentonite water content by removing the geotextile components and (b) conversion of homionic NaMt water content data into bentonite water content by including non-swelling minerals, as described below.

Conversion of GCL VET water content data into bentonite water content

The cover and carrier geotextiles masses can be subtracted from the GCL mass to obtain the bentonite mass within a given GCL sample. Knowing the mass per unit area of the geotextiles (M\textsubscript{GU} and M\textsubscript{GCL}) (Table 1) and the specific diameter of the samples used in the work reported by Acikel (2016); Rouf et al. (2016) and Bouazza et al. (2017a) allows the estimation of the mass of GCL and GT and then the obtention of the corrected GWC from:

$$W_{Bt} = \frac{W_{exp} \times M_{GCL}}{100 \times M_{GCL} - M_{GTX}} \times 100$$

(3)

where $W_{Bt}$ is the corrected gravimetric water content of the bentonite, $W_{exp}$ is the GCL gravimetric water content, $M_{GCL}$ is the mass of GCL, and $M_{GTX} = M_{GU} + M_{GL}$ (the needle punched fibres being considered part of the cover geotextile).

Conversion of homionic NaMt INS and VET water content data into bentonite water content

The water content conversion was made based on the mineralogical information provided in Table 3. The average density of non-swelling minerals, taken here as 2.55 g/cm\textsuperscript{3} from Rouf et al. (2016), is invariant with hydration. Thus a correction ratio for the INS and VET tests on NaMt can be obtained from the percentage of non-swelling materials removed. The corrected GWC is calculated from:

$$W_{Bt} = W_{exp} \frac{\rho_{Mt}}{\rho_{ns}} \times 100$$

(4)
where \( \rho_{Mt} \) is the dry density of the NaMt and \( \rho_{ave}^{ns} \) is the average dry density of the non-swelling components of the bentonite (Table 3).

Figure 4 compares the corrected data obtained from the various experiments on NaMt and GCLs. The previous investigations used conventional techniques such as VET (Rouf et al. 2016) and chilled mirror technique, CM, (Acikel 2016; Bouazza et al. 2017a; Acikel et al. 2018b). High degree of agreement between GCL data and INS is observed, especially for suction <200 MPa. For suctions >200 MPa, a difference of \( \approx 3\% \) GWC appears among GCL data and INS results. The apparent difference might be related to the errors associated with the conversion procedures stated above. The conversion indicated in Eq. 4 is based on average mass and density of mineral phases from literature. Moreover, the average mass composition of the mineral components is used in Eq. 3. Both methods introduce errors that would systematically increase as the amount of water decreases. Additionally, there is insufficient data at the highest suction for the traditional methods in the studied GCL.

CONCLUSIONS

Neutron spectroscopy experiments were carried out on the clay mineral component of a commercial GCL to obtain the dehydration/hydration behaviour at high suctions and to compare these results with those from traditional measurements on bentonites and GCLs. Based on the results, the following conclusions were made:

(a) Neutron spectroscopy results of WRC results show good agreement with traditional methods (VET) for suctions >10 MPa, which were obtained in few days compared with months that traditional methods require.

(b) While traditional methods assess water in samples as a whole, different water populations can be distinguished by neutron spectroscopy. In fact, in this paper, water populations such as bulk-like, confined and immobile water, as well as structure OH, observed within the time window of the instrument could be discerned. This differentiation is most advantageous at high suction levels, where water occupies the interlayer space of the Mt.

(c) WRC results from neutron spectroscopy were compared with GCL literature results using a conversion method derived from the material properties. Despite the assumptions and simplifications necessary in the conversions to account for non-
swelling components, the INS data displayed good agreement with literature results and can be useful for application in future studies in other commercial GCLs.

ACKNOWLEDGEMENTS

The Australian Research Council’s Linkage Projects scheme (project number LP140100516) and Geofabrics Australasia Pty. Ltd., funded this research. The Peruvian National Program of Scholarships and Student Loans (PRONABEC) are thanked for funding the first author. HNB acknowledges the support from The Danish Agency for Science, Technology and Innovation through DANSCATT. Staff at the Australian Nuclear Science and Research Organization (R. Mole, G. Iles, A. Klaproth, S. Lee, N. Booth and A. Manning) are acknowledged for their assistance.
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Figures Caption

**Figure 1.** Example of a quasi-elastic neutron scattering (QENS) spectra for a wet clay-water system where the total QENS is represented by the populations underneath the solid black line. The total scattering can be analysed using three different Lorentzian functions each representing different contributions convoluted to a Gaussian function representing the instrument resolution (Bordallo et al. 2008). Water can be discerned as different water populations within the montmorillonite: bulk-like water with different mobility (bulk-like water 1 and 2) and confined water. The three water populations compose the quasielastic signal of the sample. Immobile protons are observed within the instrument resolution as an elastic signal, which generally describes the (a) dry clay particles (b) the structural hydroxyl component and (c) a small amount of immobile water.

**Figure 2.** Total, elastic (immobile water) and quasi-elastic (mobile water) signals from inelastic neutron scattering (INS) at each applied RH step (values below data points) versus time.

**Figure 3.** WRC (in GWC values) obtained from the inelastic neutron scattering (INS) experiment compared with results obtained from the VET experiments.

**Figure 4.** Comparison of data obtained from INS and VET experiment with GCL data in other investigations using VET (Rouf et al. 2016) and chilled mirror technique, CM (Acikel 2016; Bouazza et al. 2017a).
Table 1. Physical properties of GCL used in the current study.

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<th>Property</th>
<th>Units</th>
<th>Values</th>
<th>Standard Deviation</th>
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<tr>
<td>As-received gravimetric water content</td>
<td>%</td>
<td>8 ~ 10</td>
<td>0.65</td>
</tr>
<tr>
<td>$M_{GCL}$ (@ as received gravimetric water content)</td>
<td>kg/m²</td>
<td>4.41 ~ 5.30</td>
<td>0.32</td>
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<tr>
<td>$M_b$ (@ as received gravimetric water content)</td>
<td>kg/m²</td>
<td>3.62 ~ 4.68</td>
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<td>Cover geotextile (PP) Type</td>
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<td>NW</td>
<td></td>
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<tr>
<td>Mass per area, $M_{GU}$</td>
<td>kg/m²</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>Thickness</td>
<td>mm</td>
<td>2.53 ~ 2.65</td>
<td></td>
</tr>
<tr>
<td>Standard Deviation</td>
<td></td>
<td>0.06</td>
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<tr>
<td>Carrier geotextile (PP) Type</td>
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<td>Mass per area, $M_{GL}$</td>
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<td>Thickness</td>
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<td>Bonding process</td>
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W, Woven; NW, Nonwoven; PP, Polypropylene.

Table 2. Geotechnical properties of the bentonite from the GCL used in the current study.

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<th>Property</th>
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<td>As-received gravimetric water content</td>
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<td>Liquid Limit (ASTM-D4318)</td>
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<td>Plastic limit (ASTM-D4318)</td>
<td>%</td>
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<td>Free swell index (ASTM-D5890)</td>
<td>ml/2g</td>
<td>33</td>
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Table 3. Mineralogy of the bentonite from the GCL used in the current study.

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<tr>
<th>Mineral component*</th>
<th>Mass %</th>
<th>Mass fraction $^\wedge$</th>
<th>$\rho_i$ g cm$^{-3}$</th>
<th>$y_i/\rho_i$ cm$^{-3}$</th>
<th>$\rho_{ave}$ g cm$^{-3}$</th>
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<td>Smectite$^\dagger$</td>
<td>74</td>
<td>0.538</td>
<td>2.72</td>
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<tr>
<td>Quartz</td>
<td>14</td>
<td>0.308</td>
<td>2.33</td>
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<tr>
<td>Cristobalite</td>
<td>8</td>
<td>0.154</td>
<td>2.69</td>
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<td>Albite/Anorthite</td>
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<td>Calcite</td>
<td>&lt;1</td>
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$^\wedge$mass fraction of nonswelling components only.

$^\dagger$ Structural formula = (Na$_{0.80}$[Si$_{7.77}$Al$_{0.23}$][Al$_{3.10}$Fe$_{0.30}$Mg$_{0.61}$] O$_{20}$(OH)$_4$·YH$_2$O) (where Y can be a value between 2 and 10 under most ambient conditions (Gates et al. 2017).
Figure 1. Example of a quasi-elastic neutron scattering (QENS) spectra for a wet clay-water system where the total QENS is represented by the populations underneath the solid black line. The total scattering can be analysed using three different Lorentizian functions each representing different contributions convoluted to a Gaussian function representing the instrument resolution (Bordallo et al. 2008). Water can be discerned as different water populations within the montmorillonite: bulk-like water with different mobility (bulk-like water 1 and 2) and confined water. The three water populations compose the quasielastic signal of the sample. Immobile protons are observed within the instrument resolution as an elastic signal, which generally describes the (a) dry clay particles (b) the structural hydroxyl component and (c) a small amount of immobile water.
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