Fabric effect on hydraulic conductivity of kaolin under different chemical and biochemical conditions

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Abstract

A reasonably less permeable compacted clay liner (CCL) is critical to the long-term safety of waste containment facilities. This study experimentally investigates a variety of factors, including salinity, pH, fluctuation in permeant, permeation duration and presence of microorganisms, that are found to influence the hydraulic conductivity ($k$) of consolidated kaolin and the fabrics of suspended kaolin. Amongst these factors, a reduction in hydraulic conductivity of up to 4 orders of magnitude is obtained from the modification of the microfabrics of kaolin; a reduction of 2 orders of magnitude is brought about by bioclogging; a reduction of 1 order of magnitude is related to the concentrated Ca solution ($>10$ mM). The hydraulic conductivity of consolidated kaolin can obviously be changed by adjusting the fabrics of the kaolin particles, e.g., clogging the pore spaces with bioslurry, permeating them with alkaline solution, or transforming the kaolin into metakaolin. An effluent pH larger than the isoelectric point ($\text{pH}_{\text{IEP}}$) leads to a rapid reduction in $k$ until $1 \times 10^{-11}$ m/s. A 3-dimensional fabric map was established for kaolin suspension in contact with a wide range of Ca concentrations and pH levels. The fabrics of kaolin suspension are predominated by a salt concentration ($C > 2.0$ mM) and a pH solution ($C < 2.0$ mM), respectively.

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Keywords: Kaolin; Hydraulic conductivity; Fabrics; CCL; Bioclogging

1. Introduction

Landfills are an effective way of disposing of various solid wastes (Rowe, 2005). And a well-performing liner system is fundamental to the long-term safe containment of these hazardous contaminants. Compacted clay liners (CCLs) are usually designed to be located beneath the geomembranes and geosynthetic clay liners (GCLs) as a final barrier against the possible leakage of landfill leachate (Komine and Watanabe, 2010). Although the thickness of CCLs varies with the different legislative standards, it is generally required to be around 1 m. Different from GCLs, that specifically use smectite, a spectrum of clays has been successfully implemented in CCLs according to a field investigation (Benson et al., 1999). The failure of GCLs, in terms of thermal desiccation, cracks and mineral shrinkage, has been widely observed (Southen and Rowe, 2005). A thick layer of CCL can significantly improve the performance of the barrier system by reducing the risk of toxicant leakage.

The hydraulic conductivity ($k$) of a CCL is an important factor for the assessment of its applicability and durability, which has been discussed in numerous studies that have mainly focused on the clarification of possible influencing factors on the hydraulic conductivity (Barroso et al., 2006; Basheer and Najjar, 1995; Benson et al., 1999; Day and Daniel, 1985). As soil-chemical
interactions may be active for clays, hydraulic conductivity tests should be performed for a sufficient length of time in order to allow for ion exchanges (Shackelford et al., 2000). However, few studies have investigated the long-term performance of the hydraulic conductivity of CCLs.

Kaolin is a clay mineral that is stable in a wide range of solution properties. Kaolin is also a matured commercial product (Tang et al., 2009). The exploration of a new field of applications for kaolin might open opportunities for this whole industry. Kaolin has been proposed and tested for application in CCLs (Altabbaa and Wood, 1987; Boutin et al., 2010; Wang and Siu, 2006). The physical properties of kaolin, e.g., swelling and shrinkage, are negligible in normal situations. However, the microfabric of kaolinite suspension is reportedly influenced by the pore fluid composition (Chen et al., 2000). The fabric of compacted clay was found to affect its hydraulic conductivity (Acar and Olivieri, 1989) as well as its mechanical behavior (Anantanasakul et al., 2012). This provides an opportunity to control the hydraulic conductivities of CCLs by changing the microfabrics, which can be achieved via an adjustment to the solution properties. Several works have observed the dependence of the fabrics of clay minerals on both salinity (Chen and Anandarajah, 1998) and pH (Palomino and Santamarina, 2005). The fabric orientation of sand was also observed to determine the anisotropic permeability (Jeng et al., 2008). It remains unclear, however, just how these factors function together to influence the permeability.

This aim of this study is to investigate the key factors that govern the hydraulic conductivity of kaolin. Soil treatment (the calcination of kaolin and the activation with alkaline) and solution properties (e.g., chemical concentration, pH, fluctuation and bioclogging) were experimentally evaluated. The electrical conductivity and pH of the outflow were analyzed to clarify the mechanism of the chemical–clay interaction. Soil fabrics were also studied to reveal the combined influences of pH and ionic strength. Good agreements between the changes in fabric and the shifts in hydraulic conductivity of the kaolin samples are reported for the first time in this study. These positive results could mean our conclusions would be implementable in the design and construction of CCLs.

2. Experiment and methods

2.1. Characterization of soil sample

Kaolin was purchased from a commercial clay supplier in Japan. The mineral and elemental constituents of the kaolin sample were determined by XRD and EDX, respectively, via a semi-quantitative analysis (Energy Dispersive X-Ray Fluorescence Spectrometer, Shimadzu, Japan). The mineral consists of kaolinite, quartz and albite. The main elemental components are silica, aluminum and titanium oxides, as shown in Table 1. Kaolin was further calcinated at 750 °C for 4 h to become metakaolin. Metakaolin could form a gel-like cementitious body under extremely alkaline conditions (Granizo et al., 2002). The optimum water content for the compaction of kaolin was determined to be 19% by the standard Proctor test. Other fundamental parameters for kaolin and metakaolin are also listed in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>79.5</td>
<td>%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.6</td>
<td>%</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.1</td>
<td>%</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.2</td>
<td>%</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.9</td>
<td>%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.8</td>
<td>%</td>
</tr>
<tr>
<td>Others</td>
<td>0.8</td>
<td>%</td>
</tr>
<tr>
<td>pHmeq</td>
<td>5.3</td>
<td>4.1</td>
</tr>
<tr>
<td>EC</td>
<td>10.1</td>
<td>14.1 mS/m</td>
</tr>
<tr>
<td>G</td>
<td>2.2</td>
<td>–</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>12.3</td>
<td>– %</td>
</tr>
<tr>
<td>Mass percentage</td>
<td>Diameter</td>
<td>Unit</td>
</tr>
<tr>
<td>97.1</td>
<td>12.0</td>
<td>– μm</td>
</tr>
<tr>
<td>2.9</td>
<td>0.7</td>
<td>– μm</td>
</tr>
<tr>
<td>Atterberg limit</td>
<td>Plastic limit</td>
<td>33.7</td>
</tr>
<tr>
<td>Plastic limit</td>
<td>51.2</td>
<td>52.5 %</td>
</tr>
<tr>
<td>Plastic index</td>
<td>17.5</td>
<td>19.7 %</td>
</tr>
</tbody>
</table>

Five series of settling tests were carried out in parallel to obtain the average settling velocity of kaolin. The settling behavior of kaolin slurry was studied by the image analysis system shown in Fig. 1(a). A web camera was used to monitor the time-dependent variation in the height of the deposited kaolin. Photos were frequently taken and stored in a computer. The preparation of the test sample includes sampling 4.00 g of kaolin powder and mixing it with 50.0 mL of a chemical solution, thoroughly stirred, and allowed to soak overnight before the settling test was started. The results are shown in Table 1. The majority of kaolin is sized at 12.0 μm, with trace amounts of particles sized at 0.7 μm. This agrees well with one previous work (Michaels and Bolger, 1962), but is a bit larger than other similar studies (Palomino and Santamarina, 2005; Wang and Siu, 2006).

2.2. Permeation test for kaolin

The soil specimen was prepared by consolidating the kaolin into an oedometer cell. Moist kaolin with a water content of 19% was weighed (equivalent dry weight of 50.0 g), transferred into the consolidation ring and compressed under 160 kPa for days until the differential strain was less than 0.01 mm/day. Afterwards, the specimen was vacuum saturated overnight and extruded out for subsequent processing. A flexible-wall permeameter (Fig. 1(b)) was applied to test the hydraulic conductivity. Geotextile and filter paper (1/1, with filter paper placed in contact with the soil) were installed at the two ends of the soil specimen as a drainage layer. The confining pressure was maintained at 40 kPa with a constant water head of 20 kPa for permeation. All the connections were established using TYGON tubes (4 × 3.5 mm²). Caution was taken to remove the bubbles from the connection tubes and spaces between the sample and the support. The details for each test case are shown in Table 2.
The soil specimens were first permeated with distilled water for 3–5 days in order to flush out the dissolvable salts contained in the kaolin. Afterwards, CaCl₂ solutions in various concentrations (1.0 mM, 5.0 mM, 10.0 mM, 20.0 mM, 0.1 M and 1.0 M) were permeated through the kaolin specimens in parallel. The pH and electrical conductivity (EC) of the effluent were measured at regular intervals. The permeation continued until the EC and the pH of the effluent became stabilized in order to avoid an unconservatively low prediction for the hydraulic conductivities (Shackelford et al., 2000).

The influence of the fluctuation in permeant property on $k$ (case # 8) was examined by fluctuating the Ca concentration (0–6.3 mM) and the pH (7.0–11.5). The property of the permeant was adjusted by replacing the stock solution with a fresh liquid that has a required salt concentration or pH. A gradual change in the salt concentration was achieved by injecting liquid with a different salt concentration into the source solution tank using a peristaltic pump. The permeation was temporarily paused to replace the source solution with a liquid that has a slightly reduced chemical concentration, and then restarted. This process was repeated three times. Liquids were sampled at both the inlet and the outlet of the test chamber for chemical analysis and electrical conductivity (EC).

Three cases (#9–11) tested the influence of the solution's pH on the hydraulic conductivity of the kaolin specimens. The kaolin specimens used in these tests were obtained by soaking the kaolin in chemical solutions with 0.1 M HCl (pH = 1), pH buffers (pH = 7) and 0.01 M NaOH (pH = 12), respectively. The obtained kaolin slurry was formed into specimens using an oedometer. All the samples were permeated with distilled water.

2.3. Permeation test for alkaline-treated kaolin and metakaolin

Another seven cases (#12–18) were designed to study the hydraulic behaviors of the alkaline-treated kaolin and metakaolin.

Table 2

<table>
<thead>
<tr>
<th>Case no</th>
<th>Clay</th>
<th>Additive (mM NaOH/g kaolin)</th>
<th>Initial permeant liquid</th>
<th>Consolidation period (day)</th>
<th>Permeant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Kaolin</td>
<td>–</td>
<td>Distilled water (DW)</td>
<td>–</td>
<td>1.0 M Ca</td>
</tr>
<tr>
<td>2</td>
<td>Kaolin</td>
<td>–</td>
<td>DW</td>
<td>–</td>
<td>0.1 M Ca</td>
</tr>
<tr>
<td>3</td>
<td>Kaolin</td>
<td>–</td>
<td>DW</td>
<td>–</td>
<td>20 mM Ca</td>
</tr>
<tr>
<td>4</td>
<td>Kaolin</td>
<td>–</td>
<td>DW</td>
<td>–</td>
<td>10 mM Ca</td>
</tr>
<tr>
<td>5</td>
<td>Kaolin</td>
<td>–</td>
<td>DW</td>
<td>–</td>
<td>5 mM Ca</td>
</tr>
<tr>
<td>6</td>
<td>Kaolin</td>
<td>–</td>
<td>DW</td>
<td>–</td>
<td>1.0 mM Ca</td>
</tr>
<tr>
<td>7</td>
<td>Kaolin</td>
<td>–</td>
<td>DW</td>
<td>–</td>
<td>8.9 mM Ca</td>
</tr>
<tr>
<td>8</td>
<td>Kaolin</td>
<td>–</td>
<td>6.3 mM Ca</td>
<td>–</td>
<td>DW</td>
</tr>
<tr>
<td>9</td>
<td>Kaolin</td>
<td>pH 1.0</td>
<td>–</td>
<td>4</td>
<td>DW</td>
</tr>
<tr>
<td>10</td>
<td>Kaolin</td>
<td>pH 7.0</td>
<td>–</td>
<td>4</td>
<td>DW</td>
</tr>
<tr>
<td>11</td>
<td>Kaolin</td>
<td>pH 12.0</td>
<td>–</td>
<td>4</td>
<td>DW</td>
</tr>
<tr>
<td>12</td>
<td>Kaolin</td>
<td>NaOH 1.0</td>
<td>–</td>
<td>4</td>
<td>DW</td>
</tr>
<tr>
<td>13</td>
<td>Kaolin</td>
<td>NaOH 0.2</td>
<td>–</td>
<td>4</td>
<td>DW</td>
</tr>
<tr>
<td>14</td>
<td>Kaolin</td>
<td>NaOH 0.04</td>
<td>–</td>
<td>4</td>
<td>DW</td>
</tr>
<tr>
<td>15</td>
<td>Kaolin</td>
<td>NaOH 0.02</td>
<td>–</td>
<td>4</td>
<td>DW</td>
</tr>
<tr>
<td>16</td>
<td>Kaolin</td>
<td>–</td>
<td>–</td>
<td>4</td>
<td>DW</td>
</tr>
<tr>
<td>17</td>
<td>Metakaolin</td>
<td>NaOH 10.0</td>
<td>–</td>
<td>4*</td>
<td>DW</td>
</tr>
<tr>
<td>18</td>
<td>Metakaolin</td>
<td>NaOH 10.0</td>
<td>–</td>
<td>10*</td>
<td>DW</td>
</tr>
<tr>
<td>19</td>
<td>Kaolin</td>
<td>–</td>
<td>pH 11.5</td>
<td>–</td>
<td>DW</td>
</tr>
<tr>
<td>20</td>
<td>Kaolin</td>
<td>–</td>
<td>Bioslurry</td>
<td>–</td>
<td>DW</td>
</tr>
<tr>
<td>21</td>
<td>Kaolin</td>
<td>–</td>
<td>Bioslurry</td>
<td>–</td>
<td>5 mM Ca</td>
</tr>
<tr>
<td>22</td>
<td>Kaolin</td>
<td>–</td>
<td>Bioslurry</td>
<td>–</td>
<td>20 mM Ca</td>
</tr>
</tbody>
</table>

*aThis is also the curing date for metakaolin to react sufficiently with alkaline.

The soil specimens were first permeated with distilled water for 3–5 days in order to flush out the dissolvable salts contained in the kaolin. Afterwards, CaCl₂ solutions in various concentrations (1.0 mM, 5.0 mM, 10.0 mM, 20.0 mM, 0.1 M and 1.0 M) were permeated through the kaolin specimens in parallel. The pH and electrical conductivity (EC) of the effluent were measured at regular intervals. The permeation continued until the EC and the pH of the effluent became stabilized in order to avoid an unconservatively low prediction for the hydraulic conductivities (Shackelford et al., 2000).

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2.3. Permeation test for alkaline-treated kaolin and metakaolin

Another seven cases (#12–18) were designed to study the hydraulic behaviors of the alkaline-treated kaolin and metakaolin.

![Conceptual diagram of (a) image analysis system for colloidal settling test and (b) flexible-wall permeameter (Katsumi et al., 2008).](image-url)
These kaolin samples were first thoroughly mixed with a concentrated NaOH solution (1.0 M) at different mass ratios, then moistened until the optimum water content was reached, and finally subjected to consolidation under the prescribed loading. The consolidation lasted 4 days for cases #12–17. Case #18, which used the metakaolin, was consolidated for 10 days under an extreme alkaline solution condition. The following permeation tests followed the same procedures as described above.

2.4. Permeation tests for kaolin with bioclogging

Additional soil samples were laden with bioclogging by permeating microbial slurry for the purpose of establishing an effective method to improve the performance of the hydraulic conductivity of kaolin. The microbe was screened from the surface soil in a forest within a preserved park in the Eastern Mountains of Kyoto City, Japan. Planktonic microorganisms were incubated in an MRS culture media for more than one month, whose basic nutritional components were previously reported (Li et al., 2010). In this study, solid iron oxide (Fe₂O₃, yellow brown) was added to the nutrition as an electron acceptor. The incubated microbe and the nutritional solution were diluted 20 times to prepare stock microbial slurry, and then permeated through the kaolin. The latter was previously flushed with distilled water for more than one week under a water head difference of 10.0 m. After running for 10 days, the microbial slurry was replaced by distilled water or a CaCl₂ solution for different test cases. The outflow was frequently collected and measured by volume, EC and pH meters.

2.5. Settling behavior of kaolin slurry in combined solution properties

Kaolin has three fabric types, i.e., EF flocculated, FF aggregated and dispersed, which can be assessed by a sedimentation test (Palomino and Santamarina, 2005). An image analysis system (Fig. 1(a)) was implemented to investigate the fabric variation in the suspended kaolin under various aqueous conditions. Kaolin was ground by hand into a fine powder using a mortar and then sieved with 200 mesh. A glass tube (2.54 cm in diameter) was filled with 4.00 g of kaolin and 50 mL of the chemical solution with varied CaCl₂ concentrations (0–20 mM) or pHs/levels (4–12), was capped and then shaken until a uniform appearance was observed. Afterwards, the sample tubes were placed on a level shelf, at which instant a starting time of zero was designated. The suspension heights were monitored by a PC-controlled web camera over time. The settling rate of the kaolin suspension can be calculated by analyzing the variation in solid–liquid interface over time.

3. Results and discussion

3.1. Effect of solute concentration on hydraulic conductivity

Fig. 2 shows the variation in hydraulic conductivity of the kaolin with the outflow volume. Concentrated Ca solutions (cases #1–2) caused a minor increase in $k$ for the kaolin at the beginning ($1.1 \times 10^{-7}$ m/s), and a gradual decrease in $k$ ($7 \times 10^{-9}$ m/s) at pore volume numbers (PVN) > 120. The difference between the $k$ of cases #3 and 4 was negligible before the source solution was refreshed. Afterwards, the gap between them enlarged gradually over time. Fluctuations in $k$ happened after 600 PVN when the influent stock solution was refreshed. A threshold change in $k$ appeared immediately after the permeation was re-started. The equilibrium value of $k$ for case #4 ($5.0 \times 10^{-9}$ m/s) was about 10 times less than the original value. For cases #5–6, the $k$ of kaolin...
increased by 16.7% when permeated with less concentrated Ca solutions (1 and 5 mM). The hydraulic conductivity was not affected by the consistent permeation of the Ca solution or by refreshing the source solution. The permeation of the FeSO₄ solution that was employed in case #7 did not obviously affect the $k$ of the kaolin. Similar phenomena have been observed for the hydraulic conductivity of GCLs, which show an increase of 2.13 times when permeated with a weak electrolyte ($\leq 20.0$ mM Ca), but decrease to the original value (for water permeation) when permeated with a strong electrolyte ($\geq 50.0$ mM CaCl₂) (Jo et al., 2005).

Fig. 3 shows the variations in EC and pH of the effluent with PVN. No obvious change in EC was observed for any of the specimens. In pore spaces, ion exchanges are likely to happen between cations and hydroxyl functional groups, leading to a reduced pH in equilibrium. As the surface charge of clay is negative, anions are not likely to be adsorbed in the solid. Therefore, the effluent EC, which mainly indicates the concentration of anion, is expected to remain constant throughout the permeation process (Malusis and Shackelford, 2002). The pH of the influent containing CaCl₂ is measured as $7.0 \pm 0.2$. However, the pH of the effluent varies from 4.0–5.0 to 6.0–7.0 within 50 PVN, indicating the gradual equilibration of the ion-exchange reaction between Ca and the kaolin. The effluent pH decreases with an increasing Ca concentration. The shift in pH is in good agreement with the change in hydraulic conductivity.

Fig. 4(a) compares the EC of the influent and the effluent during the course of the permeation. The obvious discrepancy in EC implies the existence of interface polarization. Fig. 4(b) displays the molecular ratio of Ca/Cl in the effluent which was determined by an EDX facility. The theoretical ratio is at 0.5, which coincides with the stock solution for CaCl₂. For concentrated Ca solutions at 1.0 and 0.1 M, the ratios are found to be 0.45 and 0.3, respectively. This could be attributed to the salt rejection effect of the kaolin, which is regarded to be characteristic of microporous materials showing semi-permeable membrane behaviors. For compacted clays, the overlap of the surface double-layer restrains the effective transport space available to the solute migration, and thus, behaves such as to only permit part of the chemical species to pass through. Similar phenomena have previously been reported for kaolin (Hart et al., 2008; Heister et al., 2006). Polarization could cause additional chemico-osmotic pressure across the soil–liquid interface and contribute further to the reduction in permeant flux. This mechanism appears to be a reasonable explanation for the observed permeability decline in kaolin after a certain period of permeation.

### 3.2. Effect of fluctuation in salt concentration on hydraulic conductivity

Under field conditions, the fluctuation in salt concentration in surface water systems is ubiquitous as the systems are strongly dependent on climatic factors. We investigated the effect of a fluctuating salt concentration on the hydraulic conductivity of kaolin. Fig. 5 plots the changes in $k$, EC and pH with the PVN of the effluent. The salt concentration varied from 0 to 6.3 mM, as reflected by the ECs in Fig. 5 (23.0 mS/m mM). The hydraulic conductivity of the kaolin decreased from $6.0 \times 10^{-8}$ to $2.0 \times 10^{-9}$ m/s, with repeated salt fluctuations; it finally fell to $1.0 \times 10^{-9}$ m/s when permeated with distilled water. The fluctuation in the solute concentration, for the first time, was found to be relevant to the change in hydraulic conductivity. The change in pH in the effluent was in the range of 6.5–8.6. When the influent was replaced by distilled water, the pH first shifted to 8.0–8.5, and then returned to neutral values near 7.0. The rapid

![Fig. 3. Variation in (a) EC and (b and c) pH of effluent with increasing pore volume number.](image-url)
3.3. Effect of pH on hydraulic conductivity

Fig. 6 shows the variation in hydraulic conductivity of the kaolin prepared at various pH conditions (from the slurry state). The hydraulic conductivity of the kaolin immersed at a pH of 1.0 remained stable at $1 \times 10^{-7}$ m/s without any obvious variation over time. The other two samples that were saturated at pH levels of 7.0 and 12.0 showed a gradual decrease in hydraulic conductivities until $1 \times 10^{-9}$ m/s within 50 PVNs. The specimen prepared at a pH of 12.0 had a lower value for $k$ than the others. The pH of the effluent was found to finally equilibrate around the isoelectric point ($pH_{IEP}$) of the kaolin. The rapid shift in pH responded to a rapid reduction in hydraulic conductivity, indicating a possible relationship between these two factors.

Fig. 7 shows the results for test cases #12–18. Kaolin that is treated with a higher NaOH/soil ratio was found to have lower initial hydraulic conductivity. The minimum for $k$ occurred as $7.0 \times 10^{-11}$ m/s for kaolin with 1.0 mM NaOH/g soil, while the maximum for $k$ was related to kaolin without alkaline treatment. The continuous permeation of DW resulted in an equilibrium value for $k$ of about $1.4 \times 10^{-10}$ m/s for the k1–k4 samples. The effluent pH equilibrated around 8.0, which is above the $pH_{IEP}$ of kaolin.

The effect of curing on the hydraulic conductivity of metakaolin is worth emphasizing. The MK specimen (case #17) had an initial $k$ of $7.0 \times 10^{-10}$ m/s, which was then decreased to values less than the equilibrium value of kaolin within 12 PVN. The sample cured for 10 days showed a stable value for $k$ of $1 \times 10^{-10}$ m/s. This behavior can be explained by the slow development of the Portland reaction between the metakaolin and NaOH (Granizo et al., 2002).

3.3.1. Changing pH of permeant

Shifting the pH of the influent could result in sharp reductions in the hydraulic conductivity of kaolin, as shown in Fig. 8. This specimen was first permeated with distilled water, and then with an alkaline solution at pH$_0$ = 11.5. There was no obvious change in the hydraulic conductivity before the pH reached the face charge isoelectric point ($pH_{IEP}$) = 7.2 (Palomino and Santamarina, 2005; Wang and Siu, 2006). Even after being permeated with distilled water, the $k$ still kept decreasing by more than two orders of magnitude until very low values ($5 \times 10^{-12}$–$3 \times 10^{-11}$ m/s), close
to the reported data for geosynthetic clay liners (GCLs), were reached. The permeation of the alkaline solution resulted in a continuous increase in EC, indicating the possible dissolution of kaolin.

3.4. Effect of bioclogging on hydraulic conductivity of kaolin and its durability against salt solution

Fig. 9 shows the effect of bioclogging on the variation in hydraulic conductivity of the kaolin with PVN. The clogging of the kaolin with microbes obviously caused a decrease in its hydraulic conductivity. The $k$ of the bioclogged kaolin appeared to decrease rapidly over time at the beginning and then to level off. The minimum was observed at $6 \times 10^{-10}$ m/s, 2 orders of magnitude lower than the original reading for kaolin. Prolonging the pretreatment resulted in lower hydraulic conductivity, indicating a higher degree of bioclogging in the specimen. This is in line with the field observations: the development of bioclogging in landfill leachate collection systems was observed after 10 years of operation (Rowe, 2005).

The permeation of the salt solutions, described next, led to some deviations in the patterns of variation in $k$ from the previous stage. Differences in the Ca(II) concentrations did not lead to significant changes in $k$. A big shift in $k$ occurs immediately after switching the permeant from bioslurry to a salt solution. The further permeation of the Ca solution (5.0 and 20.0 mM) resulted in a sharp decline to the lowest value for $k$ and a gradual increase during the following stages. The hydraulic conductivity became stabilized after 200 PVN.

Indications are that the bioclogged kaolin is resistant to the influence of chemical solutions as the clogged biomass proved to be stable. This phenomenon might be attributable to the special survival mechanisms of the geobacteria. Even with a limited amount of nutrition, the microbes can maintain their fundamental metabolism (Thullner et al., 2002). When permeated with concentrated salt, the microbial cell might be lysed due to the chemosmotic effect on the cell membrane (Hand et al., 2008). We have observed increased turbidity in the outflow when the influent liquid was replaced by a salt solution, indicating the lysis of the microbes. This could explain the gradual increase in $k$ under the permeation of Ca solutions. However, the nutrition released from the cell lysis could feed other microbes that are resistant to environmental stress (Bielefeldt et al., 2004; Hand et al., 2008).

After all, bioclogging could be easily established in compacted soils by simply permeating the suspension of the biomass, which
leads to a rather low hydraulic conductivity. Laboratory tests validated the durability of the bioclogging with respect to a chemical solution. In order to produce bioclogging in the field, it is suggested that plenty of microbe-inoculated nutrients be mixed with clay and then allowed a short-term cultivation in an unsaturated condition. This would increase the investment to some extent, however, within a controllable range. The durability and long-term stability of the formed biofilm needs to be carefully inspected in advance.

3.5. Fabric of kaolin under different solution properties

The pore fluid composition greatly influences the settling rate and the sediment volume of kaolinite suspensions in terms of double-layer repulsive and attractive forces (Chen and Anandarajah, 1998; Michaels and Bolger, 1962). Fig. 10 shows the settling behaviors of the kaolin suspension in different conditions. The settling rate, \( v_s \) (cm/log(min)), can be obtained using the following formula:

\[
v_s = \frac{L_0 - L_{t_i}}{\log(t_i/t_{i-1})}
\]

where \( L_0 \) is the suspension height (cm), \( t \) is the sampling time after the start of sedimentation, and \( L_{t_i} \) is the suspension height at sampling instant \( t_i \). The data could be plotted in curves, as shown in Fig. 10(a), which only displays one series of test data. Then, parameter \( v_s \) could be predicted using the slope, following Eq. (1). Upon further plotting of \( v_s \) with pH and salt concentration \( C \), the 3D fabric map is obtained, as shown in Fig. 10(b). The projected contours on the \( C \)-pH coordinate plane are shown in Fig. 10(c). A significant reduction in \( v_s \) was observed in the region with \( C < 1.0 \text{ mM} \) and \( \text{pH} > 9.0 \). This region indicates a deflocculated fabric of kaolin. Besra et al. had similar observations, namely, that the settling rate of kaolin slurry decreased from 0.04 cm/s at \( \text{pH} \approx 5.0 \) to 0.008 cm/s at \( \text{pH} \approx 4.8 \) (Besra et al., 2000). Palomino and Santamarina (2005) observed a threshold ionic concentration for the kaolin suspension beyond which the fabric changes. Wang and Siu also reported the relationship between the pH-dependent edge charges and the interparticle forces or associated fabric formations (Wang and Siu, 2006). An edge-to-face (EF) association and a higher final sediment volume would be formed when \( \text{pH} < \text{pH}_{\text{IEP}} \) of the edge surface. A deflocculated fabric with face-to-face (FF) flocc predominates the higher pH ranges (\( \text{pH} < \text{pH}_{\text{IEP}} \)), which could form dense sediments with a face-to-face association. As reflected in Fig. 10(c), our results agree well in tendency with these recent research works.

However, previous studies mainly investigated NaCl, rather than CaCl\(_2\), as we did in this study (Chen and Anandarajah, 1998; Michaels and Bolger, 1962).
Our results indicate that the threshold value for the ionic strength, through which the fabric of the kaolin suspension was switched from FF to EF, deviates from previously reported values. For the kaolin sample used in this study, the value is determined at 2.0 mM for the CaCl₂ solution. Palomino and Santamarina (2005) reported a threshold value for NaCl of around 100–150 mM, which is within the range of data (50–150 mM NaCl) reported by Wang and Siu (2006). The calcium proved to give rise to a tendency of the kaolin to get flocculated despite the pH being higher than the edge isoelectric potential.

3.6. Discussion

3.6.1. Sorption of Ca on kaolin

Fig. 11 shows the isotherms of the Ca adsorption on kaolin. The adsorption was found to reach equilibrium within 24 h. Sorption amounts between 1 and 14 days do not vary from each other at low concentration ranges ($C_e < 400$ mg/L). At a higher temperature (100 °C), however, the sorption was obviously enhanced. The sorption of Ca on the edge of the kaolin particles provides additional positive charges to attract the adjacent layered kaolin under an electro-static force. This is likely to explain the threshold value of the Ca concentration in the fabric map of the kaolin suspension.

Fig. 12 shows the theoretical distribution of ionic species of CaCl₂ in the aqueous solution. It is found that Ca²⁺ is stable in a broad range of pH. The variation in pH is predicted to range from

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**Fig. 10.** Variation in (a) settling rate of kaolin suspension with Ca concentration and pH: time dependent behavior, (b) 3D fabric map, and (c) the projected contour in $C$-$pH$ plane ($pH_{eq}$ and pH₀ are, respectively, the initial and equilibrium pH in clay slurry).

1998; Michaels and Bolger, 1962; Palomino and Santamarina, 2005; Wang and Siu, 2006). Our results indicate that the threshold value for the ionic strength, through which the fabric of the kaolin suspension was switched from FF to EF, deviates from previously reported values. For the kaolin sample used in this study, the value is determined at 2.0 mM for the CaCl₂ solution. Palomino and Santamarina (2005) reported a threshold value for NaCl of around 100–150 mM, which is within

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**Fig. 11.** Adsorption isotherm of Ca on Kaolin at various equilibration durations and temperatures.

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**Fig. 12.** Ionic species of CaCl₂ in aqueous solution at various pH levels and variation in pH with Ca/Cl ratio (Calculated by Visual MINTEQ, a chemical software based on thermodynamic principle; 0.10 M CaCl₂, 25 °C).
2.0 to 7.0 when the Ca/Cl\textsubscript{2} ratio increases from 0.90 to 1.0. This is in agreement with the observed effluent pHs, which were as low as 4.0 at the beginning of the Ca permeation. From Fig. 4(b), we see that the Ca/Cl\textsubscript{2} ratio stabilizes at 0.90, but the pH is equilibrated around 6.0, deviating from the predicted one (2.0). This is likely to be because the exchanged cations from the kaolin, like Mg and Na, can largely supplement the charge balance, and therefore, lead to an increase in the equilibrium pH.

### 3.6.2. Clogging on drainage layer

Fig. 13 shows the SEM images of the filter paper before and after permeation test case #16. After weeks of permeation with DW, the filter paper in contact with the kaolin specimen was found to be clogged with fine particles. The clogging mass has diameters less than the pore size of the filter paper. This clogging, which gives rise to the permeation resistance for kaolin (Li et al., 2011), could be related to the change in microfabric of the kaolin when pH > pH\textsubscript{IEP} (Fig. 7). The fine particles are supposed to be movable in soil through the macropores, and finally deposited onto the filter paper.

### 3.6.3. Role of deflocculation

Kaolin is most likely to become deflocculated due to its low plasticity index compared to other clay minerals. For poorly graded soils, e.g., kaolin-sand mixtures (clay fraction of 5.0%), the clay dispersion was found to increase the hydraulic conductivity (Frenkel et al., 1992). However, the reverse was observed in this study. Due to the absence of skeleton grains (sand) in the kaolin specimens used in this study, the erosion of fine particles appears to be impossible. The deflocculated portion of kaolin, possessing a smaller grain size than the clay aggregate (Michaels and Bolger, 1962), would result in the clogging of the pore spaces (Hand et al., 2008). The deflocculated portion of kaolin could be precisely determined by measuring the respective weight of the soil in suspension and the sediment in the settling test. We found that 3.0% of the kaolin can be deflocculated, which is a limited amount compared to a multi-swellable kaolin (Palomino and Santamarina, 2005). However, it is these fine grains that play a vital role in the adjustment of the hydraulic conductivity.

The importance of the microfabric has been recognized in previous studies, indicating that the most important variable influencing the permeability of clays is the flocculation of the clay particles, which influences the distribution of the void sizes and shapes (Mesri and Olson, 1971). The mechanical variables governing the permeability of clay are believed to include the size, the shape and the geometrical arrangement of the clay particles. This study expands this view by examining the effect of the chemical concentration, the pH and their variation on the rearrangement of the deflocculated fine particles. For kaolin, the deflocculated fabric helps maintain a very low hydraulic conductivity. We showed that the fabric change for kaolin is not recoverable if modified by chemicals or microbial activities, which partly addresses concerns about the reliability of kaolin for implementation in landfill liners.

Fig. 14 shows the relationship between the hydraulic conductivity of kaolin and its void ratio. These data are selected from several previous studies on compacted kaolin (Abdul et al., 1990; Boynton and Daniel, 1985; Mesri and Olson, 1971; Michaels and Lin, 1954; Shackelford and Redmond, 1995) and sand-kaolin mixed soil (Aringhieri and Giachetti, 2001; Chiu and Shackelford, 1998). The sand-kaolin mixed soil samples generally have higher k than kaolin, regardless of their void ratios. We note that different kaolin samples can have different conductivity performances, e.g., the Georgia kaolin appears to have much less conductivity (Boynton and Daniel, 1985; Mesri and Olson, 1971; Shackelford and Redmond, 1995) by two orders of magnitude compared with the others (Abdul et al., 1990; Michaels and Lin, 1954). Mesri and
Olson (1971) found that the void ratio can control the hydraulic conductivity, with a reduction in \( k \) of 1–2 orders of magnitude when \( e \) decreases from 1.6 to 0.8. However, our results show that reductions in \( k \) of 3–4 orders of magnitude are achievable by an adjustment to the microfabrics, which is of greater significance compared to the effect of compaction.

4. Conclusions

(1) Permeation tests indicated that the hydraulic conductivity of kaolin was decreased by 1 order of magnitude for concentrated Ca solutions \( (C_0 \geq 0.01 \text{ M}) \), but tended to increase by 16.7\% for dilute Ca solutions \( (C_0 \leq 5.0 \text{ mM}) \). Salt filtration across the soil specimen was confirmed by the difference in ECs in the influent and the effluent, which could induce chemico-osmotic pressure, and thus, reduce the hydraulic conductivity.

(2) Fluctuation in the chemical concentration resulted in a consistent decrease in the hydraulic conductivity of the kaolin from \( 6.0 \times 10^{-8} \) to \( 1.0 \times 10^{-11} \text{ m/s} \). The pH shift in the influent resulted in a sharp reduction in \( k \) by more than 2 orders of magnitude to \( 2 \times 10^{-11} \text{ m/s} \).

(3) Bioclogging could greatly improve the barring performance of kaolin by decreasing the \( k \) of natural kaolin by two orders of magnitude. Bioclogging also proved to be durable against severe environmental conditions even with concentrated salt solutions.

(4) Kaolin demonstrates low values of \( k \) under various fluidic conditions (broad range of EC and pH). Alkaline-treated kaolin and metakaolin appear to have low hydraulic conductivity \( (1.5 \times 10^{-10} \text{ m/s}) \) that satisfies the standard for landfill liners.

(5) The influences of the pH and the Ca concentration on the flocculation of the kaolin suspension were systematically investigated, and a 3-D fabric map for kaolin slurry was obtained. The deflocculated fabric is responsible for the reduction in hydraulic conductivity of the kaolin; therefore, the conductivity variation in kaolin can be assessed by a fabric map.

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