REDOX EFFECT ON THE HYDRAULIC CONDUCTIVITY OF CLAY LINER

MASASHI KAMON\(^\text{ii}\), HUYUAN ZHANG\(^\text{iii}\), TAKESHI KATSUMI\(^\text{iv}\) and NAOKI SAWA\(^\text{v}\)

ABSTRACT

Microbial activities can be enhanced by organic rich leachate occurring in solid waste landfills, which possesses the potential to alter the barrier capacity of clay liners. Flexible-wall hydraulic conductivity tests are conducted to investigate the effect of the microbial activities on the hydraulic conductivity of Osaka marine clay used for clay liners of offshore solid waste landfill sites in Japan. Permeants with different redox potentials are employed to investigate the redox effect; and, permeants with high nutrients are used to check the effect of the microbial production in soil specimens. Test results indicate that there are no obvious changes in the free swell index, the liquid limit, or the hydraulic conductivity of the marine clay when a strong reducing agent is used. When nutrients are applied for the growth of microorganisms, however, a decrease in hydraulic conductivity, ranging from greater than two orders of magnitude to less than one order of magnitude, is observed. The formation of biofilm and anaerobic inorganic precipitation on the surface of the soil particles is considered to be responsible for this reduction in hydraulic conductivity. Test results reveal that microbical activities, enhanced by landfill leachate, may not cause an increase in the hydraulic conductivity of natural clay liners of offshore landfill sites.

Key words: (hydraulic conductivity), (landfill), marine clay, (microorganisms), (redox reaction) (IGC: B0/B12)

INTRODUCTION

Clay liners are widely used as containment barriers of solid waste disposal facilities (Rowe et al., 1995; Manas-sero et al., 2000). The effectiveness of the barriers is determined by low hydraulic conductivity to the water, the organic compounds and dissolved inorganic chemicals in the leachate over long periods of time. Many studies have been conducted on the clay-chemical interactions and the hydraulic conductivity of clay liners (e.g., Shackelford, 1994; Mitchell and Madsen, 1987). Among several factors, the effect of the reduction-oxidation (redox) condition is a significant concern, because the kinds of microbial activities which are occurring at landfill sites is of utmost significance.

Leachate from landfills is usually rich in dissolved organic matter, and it can be consumed by microorganisms as a carbon source for energy. This consumption, generally, results in a great increase in the microbial population, and consequently, in a complete shift of the redox environment from aerobic to anaerobic. When leachate leaks into groundwater, a sequence of redox zones in the plume of landfills is formed (Christensen et al., 1994). Few research works have been conducted, however, on how the microbial processes affect the hydraulic conductivity of the clay liners. For the coastal landfill facilities that have been constructed to contain municipal and industrial wastes in Japan, particularly in the Tokyo and Osaka Bay areas (Aburatani et al., 1996), natural marine clay layers are employed to prevent pollutant migration. In such cases, whether or not the microbial processes enhanced by landfill leachate can actually alter the hydraulic conductivity of the marine clay liners has become a great concern. In this study, flexible-wall permeameter tests are performed to investigate the effects of both the redox potential and the microbial activity on the hydraulic conductivity of Osaka marine clay used for landfill bottom liners.

BACKGROUND

In waste materials the organic fraction will begin to undergo degradation through chemical and microbiological activities. Simply, landfill life can be divided into aerobic
Redox reactions occur simultaneously in the soil-water system. A redox reaction can be considered as a pair of coupled half reactions. Both half reactions involve the transfer of electrons between the chemical species in the system. The redox potential (Eh) of the natural soil and the sediments, as an expression of the electron density of the systems, varies widely from approximately +500 mV (surface soil) to approximately −300 mV (strongly reduced soil). Four typical ranges of redox conditions, suggested by Patrick and Turner (1968), are encountered at pH 7, namely, above +400 mV for oxidized soils, +400 to +100 mV for moderately reduced soils, +100 to −100 mV for reduced soils, and −100 to −300 mV for highly reduced soils.

Ordinarily, the redox state of a soil is closely related to the microbial activity and to the type of substrate available to the organisms. Oxidized conditions in soils are normally found in well-drained soils as well as in soils that have not been subjected to contamination by spills or leaks. Analysis on the redox conditions in paddy soils, swamp and marsh soils, and lake and marine sediments shows that reduced soils are characterized by (1) water saturation, (2) an absence of molecular oxygen, (3) anaerobic microbial activity, and (4) bio-availability of organic compounds. Both theoretical analysis and practical monitoring results show that anaerobic respiration or reduced conditions prevail in landfills and within landfill leachate plumes (Christensen et al., 2001).

Chemical reduction tests conducted by Stucki et al. (1984b) showed that the structural iron within clay minerals could be reduced; this results in the collapse of the clay layers. Wu et al. (1988) proved that, similar to what has occurred in chemical reduction tests, bacteria could also biologically reduce structural iron in clay minerals and this results in a partial collapse of the clay layers. Furthermore, a reduction in the structural iron alters many physicochemical properties of clay, such as swelling (Stucki et al., 1984b), cation exchange and fixation capacity (Stucki et al., 1984a), specific surface area (Lear and Stucki, 1989; Kostka et al., 1999), and hydraulic conductivity (Shen et al., 1992). Shen et al. (1992) performed chemical reduction tests and indicated that clay permeability tends to increase after the structural Fe(III) in the clay minerals has been reduced to Fe(II).

The effect of microbial activities on the hydraulic conductivity of soils was investigated as early as 1947, when Allison (1947) revealed that decreases in hydraulic conductivity are attributed to the biological clogging of soil pores by microbes. Seki et al. (1996, 1998) clarified through laboratory column tests that bacterial clogging, fungal clogging, and the clogging of gas produced by microbial activities are responsible for the reduction in hydraulic conductivity. Dennis and Turner (1998) studied the hydraulic conductivity of compacted silty sand treated with bacteria, and found that decreases in hydraulic conductivity from $10^{-5}$ to $10^{-6}$ to $10^{-8}$ cm/s are caused by microbial activities. Bacterial treatment was suggested as a feasible technology for creating waste containment barriers in soil.
Table 1. Properties of the Osaka marine clay used

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle density (g/cm³)</td>
<td>2.72</td>
</tr>
<tr>
<td>Natural water content (%)</td>
<td>100.4</td>
</tr>
<tr>
<td>Liquid limit (%)</td>
<td>93.3</td>
</tr>
<tr>
<td>Plastic limit (%)</td>
<td>26.6</td>
</tr>
<tr>
<td>Grain size distribution (%)</td>
<td></td>
</tr>
<tr>
<td>Gravel fraction (&gt; 2 mm)</td>
<td>0</td>
</tr>
<tr>
<td>Sand fraction (2 mm – 0.075 mm)</td>
<td>2.1</td>
</tr>
<tr>
<td>Silt fraction (0.075 – 0.005 mm)</td>
<td>52.1</td>
</tr>
<tr>
<td>Clay fraction (&lt;0.005 mm)</td>
<td>45.8</td>
</tr>
<tr>
<td>pH measured in suspension</td>
<td>7.52</td>
</tr>
<tr>
<td>pH measured in pore water</td>
<td>7.39</td>
</tr>
<tr>
<td>Eh measured in suspension (mV)</td>
<td>-377</td>
</tr>
<tr>
<td>Total organic carbon (TOC) (%)</td>
<td>0.63</td>
</tr>
</tbody>
</table>

The above literature review indicates that microbial activities exert various influences on soil behavior and soil properties. The aim of this research is to investigate microbial effects on the hydraulic conductivity of clay liners of landfill sites. In fact, microbial activities in polluted soil-water systems are extremely complicated even from a geotechnical viewpoint, and are characterized by a great increase in microbial population and a series of physicochemical reactions induced by microbial metabolism. This research focuses only on redox potential and microbial growth by designing two types of hydraulic conductivity tests, namely, hydraulic conductivity tests with a chemical reduction in which a strong reducing agent, sodium dithionite, is used to obtain a low redox potential, and hydraulic conductivity tests with microbial cultivation in which nutrients are applied to enhance the microbial activity.

MATERIALS AND METHOD

Free Swell Tests

Free swell tests are conducted to investigate the swelling properties of marine clay under different redox conditions using distilled water, sodium sulfate, and sodium dithionite as dispersing agents; they are also used as permeating solutions in the hydraulic conductivity tests as described later. Two grams of powdered air-dried marine clay minerals (passed through a 0.1 mm sieve) are carefully dusted over the surface of the 100 mL solution to allow the clay minerals to hydrate completely. After 72 hours, the final volume of the settled clay is recorded. The solutions used before the swell tests and the supernatant suspension after the swell tests are measured for pH, redox potential (Eh), dissolved oxygen (DO), and electrical conductivity (EC).

Liquid Limit Tests

Liquid limit tests on Osaka marine clay are performed according to JGS 0141-2000, and distilled water, sodium sulfate, and sodium dithionite solutions are used as pore liquids. The pore liquids are mixed with air-dried marine clay, and each mixture is separated into two portions. One is used to measure the liquid limit immediately, while the other portion is kept in a sealed container for 24 hours until the next liquid limit test.

Hydraulic Conductivity Tests with a Chemical Reduction

The marine clay material used for the experiments is sampled from Osaka Bay. The basic properties of the clay are shown in Table 1.

Hydraulic conductivity tests with a chemical reduction are conducted on the consolidated marine clay specimens, 6 cm in diameter and about 4 cm in height, using a flexible-wall permeameter. The marine clay, which has a natural water content, is consolidated with an oedometer under a consolidation pressure of 200 kPa, representing an approximate overburden pressure of disposed solid waste at a 20 m depth. The clay is then set in a flexible-wall permeameter, as shown in Fig. 2, to begin the hydraulic conductivity tests.

To compare the effect of the redox potential on the hydraulic conductivity, sodium dithionite (Na₂S₂O₄) or sodium sulfate (Na₂SO₄) is dissolved in selected influents. Sodium dithionite has been used as a strong reducing agent, while sodium sulfate, which does not alter the original redox condition, provides the same sodium ionic strength as sodium dithionite. Distilled water is used as a control test. Two types of gases, N₂ and O₂, are used as pressure gas sources to investigate whether or not the gases considerably alter the redox condition of the per- meants over the long test duration. A water head difference of 100 kPa across the specimen is applied. Other experimental conditions are summarized in Table 2.

Hydraulic Conductivity Tests with Bacterial Cultivation

Hydraulic conductivity tests with bacterial cultivation are conducted on the specimens compacted from a mixture of 80% (weight/weight) dried Osaka marine clay and
20% quartz sand, with or without Fe-coating. In fact, mixing of clay and sand is a method widely used to optimize the hydraulic conductivity of a compacted clay liner in both laboratory research and constructions of prototype liners. In this test, addition of coated sand to the marine clay is mainly employed to enhance the Fe(III) as an electron acceptor for redox reactions during the hydraulic conductivity tests.

Natural Osaka marine clay, as indicated in Table 1, is dried at 45°C for 48 hours, ground, and then sieved through a 0.1 mm sieve for specimen preparation. An iron coating is made on the surface of commercially obtained quartz sand, called Toyoura sand, according to the following procedure. One kg of quartz sand (99% within the range of 0.1–0.4 mm in particle size) is soaked in pH = 1.0 HCl for one week, and then is rinsed with distilled water. A three hundred mL solution of amorphous Fe(III)-hydroxide is freshly prepared by dissolving 34.5 g of FeCl₃ in 1 L of distilled water and then slowly adjusting the pH to 7 using 5 M of NaOH. The Fe(III)-hydroxide-sand mixture is shaken for 4 hours under 200 rpm and is then allowed to settle for several hours. The overlying water is then decanted and replaced with a 0.1 mM NaCl-solution and allowed to settle again for 12 hours. The Fe(III)-hydroxide-NaCl solution is then discarded completely and replaced with a freshly made Fe(III)-hydroxide solution. This whole process is repeated three times before the coated sand is allowed to air dry. The resulting mineral coating contains 1.34 ± 0.12 mg of Fe per gram of sand, 95% of which is Fe(III) (Gerlach et al., 1998).

Eighty percent of the dried marine clay and 20% of the quartz sand, with or without Fe-coating, are mixed. This is followed by the addition of distilled water to obtain the desired water content of w = 20%. The soil mixture is compacted with a standard Proctor hammer in a cylindrical steel mold, 10 cm in diameter, with 25 blows per lift. Table 3 shows the measured dry densities and water contents of the compacted specimens used in the hydraulic conductivity tests. In addition, Table 3 shows the permeating agents used in each hydraulic conductivity test, where 1000 ppm of zinc acetate, CH₃COOZn, and 100 ppm of ammonium dihydrogenphosphate, (NH₄)₂H₂PO₄, are added as nutrients to supply bacteria with carbon, nitrogen, and phosphorous. Various other components, such as sulfate and nitrate, are enhanced to provide electron acceptors for possible redox reactions, while hydrochloride is added to provide the same ionic strength to the sodium.

A flexible-wall permeameter, similar to that shown in Fig. 2, is used to conduct the hydraulic conductivity tests with bacterial cultivation, except that the specimens have a larger diameter (10 cm) and the falling head method is used. After the compacted specimens, 10 cm in diameter and about 3 cm in height, are placed in the permeameter cells, a confining pressure of 300 kPa is applied, followed by the application of an initial water head of 1.35 m to induce an upward flow in the specimens. The falling water head in the standpipe is recorded to calculate the influent value. Effluent coming out from the specimens is collected in a closed plastic bottle by connecting the effluent outlet to a small opening on the cap of the bottle, which is initially flushed with nitrogen gas to maintain a nitrogen

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Initial water content (%)</th>
<th>Dry density (g/cm³)</th>
<th>Permeating agent</th>
<th>Pressure gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Consolidated marine clay</td>
<td>59.8</td>
<td>1.65</td>
<td>Na₂S₂O₄</td>
<td>N₂</td>
</tr>
<tr>
<td>Consolidated marine clay</td>
<td>59.7</td>
<td>1.65</td>
<td>Na₂SO₄</td>
<td>N₂</td>
</tr>
<tr>
<td>Consolidated marine clay</td>
<td>62.0</td>
<td>1.64</td>
<td>H₂O</td>
<td>N₂</td>
</tr>
<tr>
<td>Consolidated marine clay</td>
<td>58.2</td>
<td>1.66</td>
<td>Na₂S₂O₄</td>
<td>O₃</td>
</tr>
<tr>
<td>Consolidated marine clay</td>
<td>61.7</td>
<td>1.64</td>
<td>Na₂SO₄</td>
<td>O₃</td>
</tr>
<tr>
<td>Consolidated marine clay</td>
<td>59.6</td>
<td>1.65</td>
<td>H₂O</td>
<td>O₂</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test number</th>
<th>Composition (w/w)</th>
<th>W (%)</th>
<th>ρₕ (g/cm³)</th>
<th>pH</th>
<th>Eh (mV)</th>
<th>EC (mS/cm)</th>
<th>CH₃COOZn (ppm)</th>
<th>NH₄H₂PO₄ (ppm)</th>
<th>Others chemicals (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td>80% M + 20% S¹</td>
<td>19.9</td>
<td>1.50</td>
<td>5.9</td>
<td>337</td>
<td>1.214</td>
<td>1000</td>
<td>100</td>
<td>1000 (Na₂SO₄)</td>
</tr>
<tr>
<td>No. 2</td>
<td>80% M + 20% S²</td>
<td>19.9</td>
<td>1.55</td>
<td>6.1</td>
<td>211</td>
<td>1.619</td>
<td>1000</td>
<td>100</td>
<td>1000 (NaCl)</td>
</tr>
<tr>
<td>No. 3</td>
<td>80% M + 20% S²</td>
<td>19.9</td>
<td>1.53</td>
<td>5.5</td>
<td>334</td>
<td>1.180</td>
<td>1000</td>
<td>100</td>
<td>1000 ppm (NaNO₃)</td>
</tr>
<tr>
<td>No. 4</td>
<td>80% M + 20% S²</td>
<td>19.9</td>
<td>1.55</td>
<td>5.8</td>
<td>316</td>
<td>1.193</td>
<td>1000</td>
<td>100</td>
<td>1000 ppm (Na₂SO₄)</td>
</tr>
</tbody>
</table>

M: 45°C dried Osaka marine clay, S¹: clean quartz sand, S²: quartz sand coated with Fe(OH)₃
atmosphere inside. Accumulated effluent is measured for pH, Eh, and EC, followed by the analysis of the total organic carbon (TOC) using a total organic carbon analyzer (TOC-5050, Shimadzu). The filtered effluent collected through a syringe filter with a 0.45 μm pore size is analyzed for cations by inductively coupled plasma atomic emission spectrometry (ICP-AES).

RESULTS AND ANALYSIS

Redox Control by Dithionite

The reduced conditions induced by the anaerobic respiration of the microorganisms in the soil systems can be simulated by a chemical method. Dithionite has been used to maintain a low Eh in soil systems by several researchers (Chen et al., 1987; Sticku, 1988; Shen et al., 1992).

The dithionite or hydrosulfite ion, S₂O₃²⁻, may be conceptualized as two sulfoxyl (SO₂⁻) radicals joined by a 2.39-Å sulfur-sulfur bond (see Fig. 3). The eclipsed conformation of the ion, in which the oxygens associated with each sulfur (S) atom are bound at rather acute angles relative to each other and in proximity to the oxygens attached to the other S atom, induces considerable strain within the ion. As a result, the S–S bond in S₂O₃²⁻ is considerably longer (and hence, weaker) than typical S–S bonds (2.00–2.15 Å). This weaker link in the S₂O₃²⁻ ion is the key to its chemical nature since the ion reversibly dissociates to form two SO₃²⁻ radicals that are highly reactive reductants.

Dithionite is a strong reductant, its standard electrode reduction potential is −1120 mV (Vanysek, 1999). As in the reactions with oxidants, cleavage of the S–S bond is required and is presumably the rate-limiting step in the process. Thus, dithionite is not stable in aqueous solutions for long periods of time.

The measured Eh in the freshly prepared dithionite solutions is as low as −500 mV. When the solutions are exposed to the air, their reducing power decreases and then disappears completely after 20 hours for the 1.0 M and the 0.1 M solutions, and after less than 4 hours for the 0.01 M solution. When dithionite is added to marine clay, the measured Eh in the marine clay sludges is lower than that of the pure dithionite solutions and persists for a longer time than dithionite solutions without soil. This means that the reducing power of dithionite is preserved and enhanced when added to the soil suspension, although the exact reason remains unknown. Thus, it is possible to maintain a low Eh in the soil system for a long duration with the addition of dithionite.

Free Swell of Marine Clay in Various Eh Agents

Table 4 and Fig. 4 show the results of free swell tests. The major differences among the three dispersing agents before the tests are that sulfate provides approximately the same level of redox potential as distilled water, but a higher ionic strength, whereas dithionite possesses almost the same ionic strength as sulfate, but provides a strong reducing condition. After the swell tests, the pH of the distilled water and the sulfate increases 1.6–2.0 pH units due to the weak alkalinity of the marine clay, while the dithionite becomes more acidic. A slight increase in the EC of the three agents indicates that some salts in the
Fig. 5. Liquid limit of marine clay with various redox agents as pore liquids

Fig. 6. Hydraulic conductivity of marine clay permeated by chemical solutions with different redox potentials where nitrogen gas is used as the pressure gas source

Fig. 7. Hydraulic conductivity of marine clay permeated by chemical solutions with different redox potentials where oxygen gas is used as the pressure gas source

Hydraulic Conductivity Tests on Marine Clay under a Chemical Reduction Condition

The results of hydraulic conductivity tests are shown in Figs. 6 and 7. The marine clay exhibits a hydraulic conductivity of lower than $10^{-7}$ cm/s, which satisfies the requirement for clay liners at municipal waste landfills according to the US Environmental Protection Agency (EPA) if the marginal difference in the hydraulic conductivity between artificially consolidated and naturally consolidated specimens is ignorable (US EPA, 1986). These low hydraulic conductivity levels can mainly be attributed to the presence of a high clay fraction in the marine clay. The test results shown in Figs. 6 and 7 indicate that there are no obvious differences in the hydraulic conductivity whether the specimens are permeated with different agents nor whether different gases are used to exert head pressure. In addition, the hydraulic conductivity values show no obvious variation for a test period as long as 80 days. It can be concluded, therefore, that the redox condition has no obvious effect in altering the hydraulic conductivity of this marine clay.

These hydraulic conductivity test results are consistent
with those from free swell and liquid limit tests. If pore liquids with different redox potentials can change the forces which govern the clay-water interaction and alter the microstructure or texture of the clay-water fabric, changes in hydraulic conductivity can be expected. Under the experimental conditions used in this study, the redox potential shows no obvious effect on the free swell or the liquid limit test results, and hence, no obvious changes in hydraulic conductivity occur.

Similar tests were conducted by Shen et al. (1992), who prepared the hydraulic conductivity test samples by suspending Na-smectite and compacting it under nitrogen gas to a gel. Distilled water, sulfate, and sodium dithionite were used to obtain different redox conditions. To consider the effect of consolidation history as well as the reduction reaction on the hydraulic conductivity, two kinds of reduction procedures were conducted by Shen et al. (1992): namely, clay was reduced in suspension and then consolidated, and clay was consolidated and then reduced by sodium dithionite. It was found that the reduction of clay in suspension, prior to the consolidation, decreased the hydraulic conductivity of smectites compared with the samples in their respective oxidized states. The increase in gel density, induced by the reduction of structural Fe in the smectite, was considered to be responsible for this decrease in hydraulic conductivity. When the oxidized clay suspensions were consolidated first and then reduced by dithionite, their hydraulic conductivities increased significantly compared with the sample in the oxidized state. The later test process was thought to represent a practical possibility for use at inland landfill sites, where artificial clay liners are compacted in an oxidized condition and then gradually change to a reduced condition due to the anaerobic respiration of microorganisms.

In this study, the hydraulic conductivity tests were conducted in such a way that samples are first consolidated and then reduced during the permeating duration. Although the test procedure in this study is similar to the second method (consolidation prior to reduction) employed by Shen et al. (1992), the hydraulic conductivity obtained here shows no increase; this is different from the results obtained by Shen et al. (1992). Such a difference might be attributed to the fact that the soil samples used in the tests have different redox conditions; the smectite used by Shen et al. (1992) was in an oxidized condition. When it was exposed to reducing agents, it tended to shrink and increase in hydraulic conductivity. Unlike the smectite used by Shen et al. (1992), the marine clay used in this study exists naturally in a strongly reduced condition (e.g., the Eh measured in the soil suspension is ~377 mV) for a geological time, which is long enough to let the redox reactions in the soil-water systems reach equilibrium. Thus, even when a strong reducing agent is added, no change in the microstructure of the marine clay, and therefore, no change in hydraulic conductivity, is expected.

**Hydraulic Conductivity of Marine Clay with Bacterial Cultivation**

Figures 8 and 9 show the changes in hydraulic conductivity of marine clay with time and pore volumes of flow (PV), respectively, where nutrients are applied for microbial growth. Pore volume means the total volume of pores in a soil specimen. The pore volumes of flow (PV) are the ratio of effluent volume to the total pore volume of the specimen. Therefore, PV = 1.0 indicates that one pore volume of liquid has passed through the soil specimen. With the increase in elapsed permeating time or accumulated effluent volumes, a continuous decrease in hydraulic conductivity can be observed in all specimens, in particular for Nos. 1, 2, and 4. This is very different from the results of the hydraulic conductivity tests with a chemical reduction, as indicated in Figs. 6 and 7, where no significant flocculation is observed.

The falling head permeating method is selected in this experiment, where measured influent volumes are used to calculate the hydraulic conductivities, as shown in Figs. 8 and 9. At the initial stage of the hydraulic conductivity tests, e.g., PV < 1.0, a portion of the influent is used to
increase the saturation of the soil specimens, resulting in a higher calculated hydraulic conductivity than should exist. With the increase in soil saturation, the measured hydraulic conductivity decreases and tends to be stable. Obviously, a further decrease in hydraulic conductivity after PV > 1.0 results from microbial and/or chemical processes other than a saturation change in the soil specimens. The measured hydraulic conductivity at PV = 1.0, referred to as \( K_0 \), can simply be selected as the initial value or as a reference for the comparison of this reduction. Correspondingly, the hydraulic conductivity measured at the end of each run is defined as its final value, referred to as \( K_f \). Comparing the initial and the final hydraulic conductivities listed in Table 5, it is thought that the microbial and/or the chemical processes prompt a reduction in hydraulic conductivity ranging from more than two orders of magnitude to less than one order of magnitude, which may be put in order as No. 1 > No. 4 > No. 2 > No. 3.

Figures 10, 11, 12, and 13 show the changes in the concentrations of the main cationic elements, namely, Na, K, Ca, and Mg in the effluents from each specimen with pore volumes of flow, respectively. It is clear that the leaching of soluble ions from soil specimens dominates the early stage of the hydraulic conductivity tests, in particular before 4 PV. This is proved again by the electrical conductivity (EC) of the effluents (see Fig. 14). Electrical conductivity (EC) is a measure of the dissolved salts in a solution. The bigger the EC, the more dissolved salts are contained in the solution. The larger increase in the EC of the effluents than that of the influents as shown in Fig. 14, especially when PV < 4, indicates that much more salts in the soil specimens are dissolved and leached out by the effluent. This is consistent with the concentration changes in the main cationic elements as shown in Figs. 10, 11, 12, and 13.

The leaching of soluble components from the soil results from dissolution-precipitation and cation exchange reactions occurring in the soil-water systems. The leaching procedure may affect the hydraulic conductivity of the soil if the chemical reactions between the soil particles and the permeating solution can alter the microfabric or the arrangement of the soil particles. Theoretically, the hydraulic conductivity equilibrium can be established only after a chemical equilibrium has been reached. The leaching reaction is a process in which concentration decreases very quickly at the initial stage, but very slowly at the final stages. From a practical viewpoint, therefore,
the measured EC decreased to 5% of its initial value can be thought of as a reasonable criterion for the judgment that most of the leaching reaction has been completed. The hydraulic conductivity value corresponding to 5% of the initial EC of the effluent, referred to as $K_1$, is also listed in Table 5. Variations between $K_0$ and $K_1$, as listed in Table 5, might mainly represent the leaching effect on hydraulic conductivities, because leaching of soluble components from the soil is the major event occurring in this test duration. From Table 5, it is found that only a small part of the hydraulic conductivity reduction happens during the leaching stage for specimen Nos. 1, 2, and 4 with respect to their whole hydraulic conductivity reduction, but a larger part of the reduction happens during the leaching stage for specimen No. 3, which has the least whole reduction among the four specimens. This suggests that something other than the chemical leaching of soluble ions from the soil is mainly responsible for the whole reduction in hydraulic conductivity for specimen Nos. 1, 2, and 4.

The changes in the pH and the Eh of the effluent with pore volumes of flow, as illustrated in Fig. 15, might provide insight into the mechanism of hydraulic conductivity reduction. As can be seen in Table 4, the permeating solutions are acidic with a pH range of 5.5 ~ 6.1, whereas the effluents are alkaline and expressed an increasing pH tendency from 7.4 to near 9.0. Typical pH values of marine sediments are in the range of 7 ~ 8, which partly account for the increase in the pH of the effluents. On the other hand, the microbial activities enhanced by the nutrient application from continuous influent provide another possible cause for the increase in effluent pH.

In fact, there is an abundant distribution of native microorganisms in natural soils, including the Osaka marine clay used in this study. In a microenvironment such as that in the hydraulic conductivity test specimens, anaerobic respirations predominate because the dissolved oxygen in the permeant is consumed by microorganisms at a greater rate than it can be provided. This results in a reduced condition that can be proved by the decreased redox potentials (Eh), as shown in Fig. 15. It should be noted that the actual redox potentials in the hydraulic conductivity specimens would be lower than those indicated in Fig. 15 due to the partial oxidation of the effluent to some extent. As mentioned before, great efforts have been made to try and prevent the effluent from making contact with the air. To meet the requirements of various measurements, such as Eh, pH, EC, and the chemical analysis, sufficient volumes of effluent have to be accumulated. Usually it takes 3 ~ 4 days, but sometimes it takes as long as 1 or 2 weeks when the hydraulic conductivity becomes too low. During such a long period of time, the exposure of effluents to the air cannot be avoided, to some degree, although the bottles are closed.

Microbial activities in natural soil-water systems are closely related to the available organic carbon. The addition of organic carbon to soil-water systems may enhance the microbial activities in them. Likewise, faster consumption of organic carbon reveals increased microbial activity. The Osaka marine clay used in this study is characterized by a higher content of organic carbon,
which is capable of being partly dissolved and leached out. That is why the total organic carbon (TOC) in the effluent is higher than that in the influent at the early stage of the hydraulic conductivity tests (see Fig. 16). With the further development of the microbial activities in the soil specimens, much more organic carbon is consumed and the TOC in the effluent decreases to less than that in the influent. From the facts analyzed above, it appears reasonable to assume that the hydraulic conductivity reduction is mainly related to the microbial activities in the soil specimens.

In actuality, decreases in the permeability of porous media, caused by the growth of microorganisms, have been observed and reported in literature for over fifty years (Allison, 1947). This process is commonly referred to as "plugging", "clogging", or "fouling". Examples include sewage infiltration ponds becoming severely plugged (Mitchell and Nevo, 1964), sandstone formations becoming clogged due to bacteria present in the injected water for enhanced oil recovery (Hart et al., 1960), soil becoming clogged when wastewater is recycled by sprinkler irrigation (de Vries, 1972), incrustations forming in drain pipes and filter material, and leachate collection systems at landfill sites becoming clogged (Brune et al., 1994).

Seki et al. (1996, 1998) conducted permeability tests on soil sampled from a rice paddy field in Tokyo, Japan. A glucose solution was applied to soil specimens as a substrate for microbial growth, and different bicodiates were added to selectively kill bacteria or fungi, or both bacteria and fungi for comparison. A decrease in hydraulic conductivity was observed in all tests where bacteria and/or fungi were cultivated. After the permeant with substrate was replaced by a sodium azide solution that possibly can kill both bacteria and fungi, the decreased hydraulic conductivity began to increase, although it could not return to its initial value. The authors concluded that the reduction in hydraulic conductivity was due to biological clogging (consisting of bacterial clogging, fungal clogging, or both) and gas occlusion, even though the biological clogging mechanisms were not provided in detail.

The production of microbial gas has been observed by many researchers (e.g., Seki et al., 1996, 1998) when nutrients are applied to enhance microbial activities. To investigate if the bacterial gas is mainly responsible for the decrease in hydraulic conductivity in this research, influent and effluent volumes are carefully measured and the correlation between them is analyzed (see Fig. 17). If bacterial gas is produced, it will either be dissolved in the permeating liquid and transported out of the soil specimen with effluent, or it will occupy its space in the soil pores by driving out some liquid which previously existed there. The former mechanism would be expected to lead to a series of changes in effluent chemistry, while the latter would be expected to result in a net increase in effluent volume, to more than influent, within a certain monitoring period. As seen in Fig. 17, there is more influent than effluent and the influent/effluent ratio > 1.0 before a PV of 1.0 occurs due to the saturation of soil specimens during the initial permeating stage. After a PV of 1.0, a continuous flow is maintained for all of the specimens where the influent/effluent ratio is kept at around 1.0 without much variation (see Fig. 17). This indicates that a series of tests has reached the steady state condition, and also might suggest that bacterial gas does not interrupt the permeating flow by driving out liquid and holding space in the soil pores. Therefore, the microbial gas does not seem to be the main cause of the decrease in hydraulic conductivity.

Microbial clogging is considered to be the main cause of the decrease in hydraulic conductivity in this experiment. As for the mechanism of microbial clogging, different explanations are available. Seki et al. (1998) and Dennis et al. (1998) tended to agree with the biofilm formation. Biofilm refers to the organic material consisting of microorganisms embedded in a polymer matrix of their own making (Characklis and Marshall, 1990). After the initial colonization, the bacteria produce extracellular polymers, within which the bacterial cells are embedded. When aquatic bacteria attach firmly to the surfaces of soil
particles, biofilm forms. The formation of biofilm in a porous medium may decrease the pore volume available for fluid transport and change the shape of the pore spaces, resulting in a reduction in permeability.

Brune et al. (1994) provided a new explanation for the microbial clogging mechanism from field observations and the laboratory modeling of leachate drainage system clogging: namely, anaerobic bacteria are responsible for the formation of incrustations in drainpipes and filter material. It was found that the incrustation material consists of a network of aggregates of bacteria with deposits of precipitated inorganic material on their surfaces. The inorganic components are mainly calcium, iron, magnesium, and manganese combined with carbonate and sulfur. It is thought that sulfate-reducing bacteria and methane bacteria cause a local alkaline microenvironment in the vicinity of the bacteria by their metabolic consumption of hydrogen ions, which results in the precipitation of sulfide and carbonate on their surfaces.

The writers tend to believe that both theories of biofilm formation and anaerobic inorganic precipitation, as mentioned above, provide valuable explanations for the microbial effect on hydraulic conductivity. When nutrients are available to microorganisms in anaerobic soils, biofilm consisting of microbes and their organic by-products is formed and attaches to the surface of the soil particles, resulting in a reduction in hydraulic conductivity by decreasing the pore volume available and changing the shape of the pore spaces. If anaerobic respiration develops further to sulfate reducing and methanogenic stages, inorganic precipitation such as sulfides and carbonate will be formed on the surface of the microbes, reinforcing the biological clogging process. Using this hypothesis, the cause for No. 3 having the least reduction in hydraulic conductivity among the four specimens can be explained as described in the following paragraphs.

In soil-water systems, several redox reactions may coexist. However, microbial redox reactions occur in a sequential way, in energy yield decreasing order from oxygen reduction, nitrate reduction, and Fe(III) reduction to sulfide reduction (Stumm and Morgan, 1996). That is, one redox reaction dominates the system at one time. Electron acceptors in the hydraulic conductivity tests with microbial cultivation were enhanced by permeants and/or Fe(III)-coated sand in soil specimens (see Table 3). The major electron acceptors with high energy yield in corresponding redox reactions would be sulfite in No. 1, Fe(III) in No. 2, nitrate in No. 3, and Fe(III) in No. 4. It is reasonable to assume that the availability of the major electron acceptor in each specimen controls the corresponding redox reactions there, that is, sulfite reduction prevailing in No. 1, Fe(III) reduction in Nos. 2 and 4, and nitrate reduction in No. 3. Among these redox reactions, the reduction of nitrate, if occurring in No. 3, might lead to two visible results: a faster consumption of organic matter and a higher redox potential than that of the other specimens. Figure 16 shows the change in total organic carbon (TOC) of effluents from the specimens Nos. 1 to 4 with pore volumes of flow. A break line shown in Fig. 16 represents the TOC of influents for Nos. 1 to 4, which is the same for all influents and within the whole test duration. The fact that the TOC of effluent is greater than that of influent means an obvious dissolution and leaching out of organic matter contained in the marine clay specimens, while the fact that the TOC of effluent is lower than that of influent means a significant consumption of organic matter contained in the influent. From Fig. 16, it is observed that the input organic carbon is continuously consumed, or turned over, to inorganic carbon by microorganisms within all soil specimens. The difference among these specimens is that the consumption of organic carbon in No. 3 occurs at a higher speed than that of other specimens.

Theoretically, a nitrate reduction reaction, which is assumed to be happening in No. 3, would maintain a weaker anaerobic reduction condition in No. 3 than in the other specimens. As a result, higher redox potentials would be observed in the effluent of No. 3 than in the other specimens. However, the measured redox potentials shown in Fig. 15 fail to reflect this difference. This inconsistency may be attributed to the exposure of the effluents from Nos. 1, 2, and 4 to the air for a longer time than that from No. 3, as mentioned before. This is because Nos. 1, 2, and 4 specimens exhibit significantly lower hydraulic conductivity than No. 3 (see Figs. 8 and 9) and, therefore, it took a much longer time to collect enough volume of effluents for the Eh measurements.

The least reduction in hydraulic conductivity of No. 3 among four specimens can be explained from the difference in the reduced conditions between No. 3 and other specimens. Brune et al. (1994) performed microbiological on-growth experiments to study the incrustation problems in landfill drainage systems. It was found that anaerobic bacteria are responsible for the formation of incrustation in drain pipes and filter material. To the incrustation mechanism, Brune et al. (1994) explained that iron-reducing solubilizes Fe(III) by reducing it to Fe(II), while sulfate-reducing bacteria reduce sulfate and cause the milieu in the vicinity of the sulfate-reducing bacteria to become more alkaline, which results in the precipitation of insoluble metal sulfide on the surface of the anaerobic bacteria. The weaker reduced environment maintained by the nitrate reduction reaction in No. 3 than in the other specimens does not favor the formation of inorganic precipitations according to the anaerobic bacterial clogging theory suggested by Brune et al. (1994). Therefore, the least reduction in hydraulic conductivity in No. 3 can be reasonably expected. Indirect evidence can also be found from the filtering of effluents before the chemical analysis. When effluents are filtered through a syringe filter with a pore size of 0.45 µm, it is found that No. 3 can be done with much ease, while Nos. 1, 2, and 4 are done with difficulty, showing that No. 3 contains few colloid fractions. Based on the analysis above, it may be concluded that the significant decrease in hydraulic conductivity of Nos. 1, 2, and 4 results from the formation of biofilm and inorganic precipitation in the Fe(III) reduction and sulfite reduction conditions. In contrast, the
No. 3 specimen has a comparatively higher redox potential due to the nitrate reduction reaction in it. Such a redox condition does not prefer the formation of inorganic precipitation; therefore, there is less decrease in the hydraulic conductivity of No. 3 specimen.

PRACTICAL IMPLICATION

Landfilling of solid wastes still remains the most widely used waste management method, where bottom liners are employed as the most important barriers for prevention of pollution migration. Leachate from landfills contains many dissolved and suspended materials that are detrimental to the quality of the waters and to the geotechnical performance of clay liners. The major concern is whether or not the pollutants present in leachate may result in an increase in hydraulic conductivity. It is found that the compatibility of clay liner to leachate is related to volume shrinkage (Hettiaratchi et al., 1988). The shrinkage in compacted liners often results from cation exchange (Hettiaratchi et al., 1988), increases in salt concentrations in the solutions within the clay liner (Green et al., 1983), and the dissolution of the clay minerals by acidic and alkaline solutions present in the clay liner materials (Peterson and Krupka, 1981).

The presence of certain organic compounds in the leachate is sometimes associated with increased permeability (Green et al., 1983). However, the amount of organic compounds seems to determine the degree of impact that the clay liners experience. Daniel et al. (1988) found that solutions containing low levels of organic compound did not cause shrinkage of clay liner materials.

Microbial activity enhanced by the organic rich leachate is the most important phenomenon occurring in landfill sites. However, few research results have been published about the microbial effect on the performance of clay liners at landfill sites. Test results of this research show that there are no obvious changes in the hydraulic conductivity of the Osaka marine clay when a strong reducing agent is used. When nutrients are applied to enhance the microbial growth in hydraulic conductivity tests, anaerobic respirations occur in soil specimens, promoting the formation of biofilm and anaerobic precipitations, and therefore leading to a decrease in hydraulic conductivity. As an overall conclusion, anaerobic microbial activities do not have an adverse effect on the hydraulic performance of marine clay as natural landfill liners at offshore landfill sites in Japan.

CONCLUSIONS

From the above test results, the following conclusions can be drawn.

(1) Marine clay obtained from Osaka Bay is a strongly reduced soil, which possesses a redox potential as low as $-377$ mV. Reducing agents have no obvious effect on the liquid limit or the swell behavior of the marine clay.

(2) When Osaka marine clay is permeated with periments of different redox potentials, no obvious changes in hydraulic conductivity are observed. Therefore, Osaka marine clay is not sensitive to changes in the redox potential with respect to its hydraulic conductivity.

(3) When nutrients are applied to enhance the growth of native microorganisms in Osaka marine clay during permeability tests, a decrease in hydraulic conductivity is observed, ranging from greater than two orders of magnitude to less than one order of magnitude. The formation of biofilm and anaerobic inorganic precipitation on the surface of the soil particles is considered to be responsible for the reduction in hydraulic conductivity.

(4) Anaerobic microbial activities enhanced by the organic rich leachate from solid waste landfills show a tendency to clog clay liners, leading to a decrease in hydraulic conductivity. With respect to this point, anaerobic microbial activity does not have an adverse effect on the hydraulic performance of clay liners at landfill sites.

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