Changes in Properties of Holocene Series during Storage in Thin Wall Tube Samplers

By
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Abstract: This study aims at investigation on changes of properties on Holocene Series during storage in thin wall tube samplers. Series of laboratory testing including color analysis, concentration testing of Arsenic (As), Fluorine (F) and Boron (B) in pore water, pH, oxidation reduction potential (ORP), density of soil particles and Atterberg’s limits were performed on Holocene Series at immediately after sampling and after stored for 2 years in thin wall tube samplers. The results show that at almost the unchanged water content, color of Holocene Series was change from dark olive gray to brown and soil properties were changed as follows. Pore water concentrations of As, F and B changed arbitrarily. pH decreased from 8-9 to 4-6 in some samples. Density of soil particles decreased from 2.60-2.65 to 2.50-2.55. ORP increased from negative value to positive value which means that the condition of sample changed from reduction to oxidation. Based on these results, it is possible that the properties of Holocene Series are changed during storage due to oxidation process.

Key words: Soft Ariake clay, Storage, Thin wall tube samples, pH, ORP, Oxidation process

1. Introduction

There is a question that the soil samples after stored for months represented the in situ characteristics of soil or not. The clay samples usually are changed in color after storage. The process responsible for changes of properties during storage is referred to as “oxidation process”.

Many cases have been reported where significant changes in sensitivity, Atterberg limits, and pore water chemistry occurred during storage. Torrance(1) reported the effects, on the pore water chemistry, storage for 3 months under a wide variety of storage procedures. The soft Champlain clay with a low salinity and a sensitivity of 10-20 was used in testing. The salinity and the percentage of divalent cations in the pore water had increased. According to Torrance, the increase in the concentration of calcium and magnesium in the pore water during storage is probably related to attack on carbonates present in the soil. Lessard and Mitchell(2) also investigated the changes during storage of soft Champlain clay in 1 year period to evaluate the effect of various storage. Regardless of storage procedure, the remoulded strength, plastic limit, and liquid limit increased with time, whereas the sensitivity, the liquidity index and the pH decreased. The water content, plastic limit and undisturbed strength are remained unchanged. The pore water concentrations of calcium, magnesium, and sulfate were increased by several folds.

In order to better understand the geotechnical and chemical changes occurring in Holocene Series during storage, the testing program was carried out.

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2. Materials and Experiment Methods

2.1 Materials

The soft Ariake clay from the Ariake clay formation deposited in marine condition as specified by Hino et al.(3) was used in the testing program. The soft clay was taken by thin wall tube or split spoon samples at Fukudomi area, Saga pref ecture. Soft clay from two boreholes, BH-2 and BH-4 was sampled from ground surface down to 30 m depth. The thin wall tube samplers were waxed with paraffin prior at site to protect the soil sample in good condition. Half quantities of samples were conducted the physical and chemical testing immediately after transportation to the laboratory. Whiles the other half quantities were stored in the storage room for 2 years before testing. Properties of the Ariake clay samples are shown in Figs 1 and 2 for BH-2 and BH-4.

2.2 Experimental Methods

In this study the testing was conducted in according with the Japanese International Standard. Generally, Geotechnical property tests carried out on natural sample at immediately after sampling. Pore water chemistry test performed on both samples at initial and 2 years after storage in thin wall tube.

2.2.1 Physical properties

Physical property tests including Atterberg’s limits, natural water content, specific gravity and particle size distribution were carried out. Atterberg’s limits followed the Japanese International Standard (JIS-A1205); natural water content test followed JIS-A1203; density of soil particle test followed JIS-A1202; and particle size distribution test followed JIS-A1204.
Fig. 1 Soil properties chart of BH-2 (Fukudomi district)
Changes in Properties of Holocene Series during Storage in Thin Wall Tube Samplers

Fig. 2 Soil properties chart of BH-4 (Fukudomi district)
2.2.2 Color Analysis

Standard soil color charts are used in the color analysis. Sufficient luminance is preferred when using soil color charts. If the soil environments of the samples have not changed significantly from the time of the deposition, they generally would show a dark grey to dark bluish gray color while the oxidized samples generally trend to show brown color tone.

2.2.3 Salinity Measurement

In salinity measurements on samples that may be deposited by seawater, various components must be analyzed as the composition is derived from Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^-\), HCO\(_3\)\(^-\), and SO\(_4\)\(^{2-}\) (Ohtsubo et al.\(^{10}\)). The JGS\(^{35}\) recommends the use of flame atomic absorption spectrometry for cation and ion chromatography for anion measurements.

In an attempt to facilitate quick measurements and reduce the costs associated with salinity measurements, Hino et al.\(^{(6)}\) have proposed a simple method using a commercial salinity meter for food. Salinity meters available in Japan are either conductivity type or composite electrode type. It was found that the electrode type performs better than the conductivity type. A salinity meter that can analyze Cl\(^-\) is preferable if total salinity is to be measured, however there is no suitable commercial product that measuring in wide range of salinity.

2.2.4 pH and ORP measurements

pH measurement is based on a standard by JGS. The soil pH was measured in a 1:5 (by weight) mixture of soil and distilled water. Thirty grams (dry weight) of wet soil of known water content was used for the test. Distilled water was added to the soil to obtain a total weight of 180 g. The slurry was mixed thoroughly and then allowed to stand undisturbed for 30 min to 3 hr. After that, the pH-meter positioned in near-contact with the bottom of container and measured pH value.

A device to measure oxidation (aerobic condition) reduction (anaerobic condition) potential (ORP) can be purchased in conjunction with pH meter. A potentiometer, whose input resistance is similar to that of the mV range of the pH meter, a platinum electrode, and a comparison electrode are used for ORP measurements.

In general, a sample in aerobic condition indicates low value of ORP while sample in anaerobic condition shows high value of ORP. The measurement of ORP shall be done in short period due to quickly changing of ORP value depending pH, temperature and the sample condition which is alternated when exposing to the air. Therefore, the following measurement method is proposed in this program. Immediately after sample is split in two portions in longitudinal direction, a sensor is pushed into the sample about 1 cm for 5 min. to stabilize ORP value. In case of the fluctuated value, the average value may be adopted.

2.2.5 Pore water chemistry

The pore water used for cation determination was obtained by centrifuging with machine and dilution or by squeezing the soils in a modified hydraulic pressure apparatus. The pore water was filtered. Then, The pore water was used for the determination of cation concentrations including As\(^+\), B\(^+\) and F\(^-\) via inductively coupled argon plasma spectrophotometer (ICP) to compare with the standard requirements.

3. Results and Discussions

3.1 Oxidation process

Based on Lessard and Mitchell\(^{(2)}\), two major oxidation processes take place in the Champlain quick clay during storage: the organic matter and pyrite oxidations.

3.1.1 Organic matter oxidation

The oxidation of carbohydrates or organic matter (for example formaldehyde \(\text{CH}_2\text{O}\)) produces \(\text{CO}_2\) according to the reaction

\[
\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad [1]
\]

The increase in pressure of \(\text{CO}_2\) results in the formation of a weak acid, \(\text{H}_2\text{CO}_3\), which decreases the pH and increases the concentration of calcium and bicarbonate by dissolving calcium carbonate.

3.1.2 Pyrite oxidation

By simply explanation, the oxidation of pyrite is

\[
4\text{FeS}_2(S) + 15\text{O}_2 + 14\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 16\text{H}^+ + 8\text{SO}_4^{2-} \quad [2]
\]

In neutral or slightly acid waters, \(\text{Fe(OH)}_3\) is insoluble, and the formation of sulfuric acid will be increased which causes a decrease in pH. Sulfuric acid results in dissolution of calcium carbonate in sample. Therefore, the total salinity will be increased resulting in a decrease of interparticle forces and leads to an increase in remolded strength and liquid limit of Champlain quick clay.

3.2 Color analysis

After two years storage in thin wall tube, the color of soil samples was changed into two portions, red color from the effect of pyrite oxidation in outside portion and grey color as an original color in inside portion. The color of clay samples classified according to revised standard soil color chart (Oyama and Takehara\(^{(7)}\)) is tabulated in Tables 1 and 2 for BH-2 and BH-4.

Table 1. Color analysis on soil sample at BH-2 after 2 years storage.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Color from Color Chart</th>
</tr>
</thead>
<tbody>
<tr>
<td>From</td>
<td>To</td>
</tr>
<tr>
<td>Description</td>
<td>Code</td>
</tr>
<tr>
<td>2.20</td>
<td>2.30</td>
</tr>
<tr>
<td>4.35</td>
<td>4.45</td>
</tr>
<tr>
<td>8.35</td>
<td>8.45</td>
</tr>
</tbody>
</table>
Changes in Properties of Holocene Series during Storage in Thin Wall Tube Samplers

Fig. 3  ORP of soft clays from BH-2 and BH-4 after storage in thin wall tube (Fukudomi district)

Fig. 4  pH of soft clays from BH-2 and BH-4 after storage in thin wall tube (Fukudomi district)
Fig. 5 Soil particle density of soft clays from BH-2 and BH-4 after storage in thin wall tube (Fukudomi district)

Fig. 6 Atterberg’s limits of soft clays from BH-2 and BH-4 after storage in thin wall tube (Fukudomi district)
Changes in Properties of Holocene Series during Storage in Thin Wall Tube Samplers

Table 2. Color analysis on soil sample at BH-4 after 2 years storage.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Color from Color Chart</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>From</td>
<td>To</td>
<td>Description Code</td>
</tr>
<tr>
<td>2.35</td>
<td>2.45</td>
<td>dark olive 2.5GY</td>
</tr>
<tr>
<td>4.30</td>
<td>4.40</td>
<td>gray 3/1</td>
</tr>
<tr>
<td>6.30</td>
<td>6.40</td>
<td>brown 10YR 4/4</td>
</tr>
<tr>
<td>8.35</td>
<td>8.45</td>
<td>dark brown 10YR</td>
</tr>
<tr>
<td>10.30</td>
<td>10.40</td>
<td>brownish black 3/3</td>
</tr>
<tr>
<td>12.30</td>
<td>12.40</td>
<td>black 10YR 2/2</td>
</tr>
<tr>
<td>14.30</td>
<td>14.40</td>
<td>dark brown 10YR</td>
</tr>
</tbody>
</table>

3.3 Oxidation reduction potential (ORP)
As illustrated in Fig. 3, ORP of all soft clay samples increased from negative value to positive value. The results indicate that the condition of samples changed from reduction (anaerobic) to oxidation (aerobic) resulting in continuing of oxidation process.

3.4 pH
Fig. 4 shows the comparison of pH value at initial condition and after 2 years storage. The result indicates that pH value decreased in all samples as expected. According to equations [1] and [2], the increasing of H₂CO₃ and H₂SO₄ from oxidation process may cause low pH in soft clay after storage.

3.5 Pore water chemistry
The ion concentrations of Arsenic, Fluorine and Boron are tabulated in Table 3. These three ions are selected to examine in this study because the value of their concentrations are over standard at initial condition. However, after storage, the results show the random value of ion concentrations. The reason of the random results may be due to the difference of pore water obtained method. Pore water was obtained by centrifuge machine and dilution in initial condition. While in two year storage sample, the pore water was obtained via squeezing with hydraulic pressure machine.

3.6 Density of soil particle
The soil particle density (ρₛ) at initial condition and after 2 years storage was illustrated in Fig. 5. The results showed that the soil particle density decreased after storage in all samples similar to previous report by Koslanant (8). It is possible that biogenic pyrite in soft clay may dissolved due to oxidation process.

3.7 Atterberg’s limits
As show in Fig. 6, the Atterberg’s limits of samples are still not change significantly during 2 years storage comparing with the disturbed samples stored in the plastic bucket (Koslanant(8)). Therefore, the sample stored in thin wall tube has less effect of oxidation than the disturbed sample stored in plastic bucket.

4. Concluding Remarks
This research work concentrated on the changes of soil properties during storage in thin wall tube. Based on results the following conclusions are made:
1. The oxidation process plays important role on soil properties during storage. The process begins from the oxidation of pyrite, which results in producing of sulfuric acid. The acid causes the dissolution of calcium carbonate, which increases the concentration of divalent cation in clay, thus altering in soil properties.
2. The soil properties changed during storage due to oxidation process are as follows. The colors of samples change from dark olive gray to brown. pH decreases due to increasing of acid. ORP increasing indicates the change of environment to oxidation. Density of soil particle decreased because of biogenic pyrite dissolution.
3. Once the samples deliver to the laboratory, the testing shall be done as soon as possible. pH test shall be measured to monitor the oxidation during stored in the laboratory.

Acknowledgement
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References


