Effect of Oxidation on Liquid Limit

Member	K. Onitsuka	Saga University	Student Member	0	S. Koslanant	Saga University
Member	T. Negami	Saga University	Student Member		K. Ohtani	Saga University

I Introduction

Prior to the field construction series of tests are conducted to predict the behavior of in situ soil with and without binder(s). 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 with no change in water content 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 (1976) 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 (1985) also investigated the changes during storage of soft Champlain clay in 1 year period to evaluate the effect of various storages. 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.

However, liquid limit decreased by half of original value causing by oxidation was also recognized (Soil experiment method, 1969). In order to investigate possible reasons of the differences, the available papers were reviewed and discussed.

II Oxidation mechanism

According to Lessard and Mitchell (1985), evolution sulfate and bicarbonate concentrations with time suggests that two major oxidation processes take place in the clay during aging, namely the oxidation of organic matter and oxidation of iron sulfide.

Organic matter oxidation The oxidation of carbohydrates or organic matter (generalized here as a simple formaldehyde CH_2O) produces CO_2 according to the general reaction

 $[1] \qquad CH_2O + O_2 \quad \longrightarrow \quad CO_2 + H_2O$

In the keeping samples, CO_2 cannot escape and builds up. The increase in pressure of CO_2 results in the formation of a weak acid, H_2CO_3 , which decreases the pH and increases the concentration of calcium and bicarbonate by dissolving calcium carbonate. The oxidation of organic matter appears to be catalyzed by microorganisms such as spores or molds that show reduced activity at lower temperature.

Pyrite oxidation Based on Lissard and Mitchell (1985)'s explanation, Fig. 1 shows the various steps involved the cycle of pyrite oxidation. First pyrite is oxidized by oxidized by oxygen according to the equation

 $[2] \qquad 4FeS_{2(s)} + 14O_2 + 4H_2O \implies 4Fe^{2+} + 8H^+ + 8SO_4^{2-}$

Ferrous iron is then oxidized to ferric iron by the reaction

$$[3] \qquad 4Fe^{2+} + 4H^{+} + O_2 \rightarrow 4Fe^{3+} + 2H_2O$$

The reaction in [3] occurs extremely slowly at low pH unless it is catalyzed by bacterial. The ferric iron formed by the reaction in [3] may either participate as $Fe(OH)_3$ according to the reaction

[4] $4Fe^{3+}+12H_2O \rightarrow 4Fe(OH)_{3(s)}+12H^+$

or be available to oxidize more FeS_2 to Fe^{2+} by the reaction $4\text{FeS}_{2(s)}+14\text{Fe}^{3+}+8\text{H}_{2}\text{O} \rightarrow 15\text{Fe}^{2+}+2\text{SO}_{4}^{2-}+16\text{H}^{+}$ [5]

In neutral or slightly acid waters, 4Fe(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. The increase in salinity in pore water results in a decrease of interparticle forces and leads to an increase in remolded strength. Furthermore, Fe(OH)₃, formed during the oxidation of iron sulfide, is believed to increase the specific surface area of the clay, which result in a higher water-holding capacity, and increasing in liquid limit.



Fig.1 Mechanism of pyrite oxidation (Lessard and Mitchell, 1985)

III Discussions

It is interesting that why some soils in Ariake area show the decrease in liquid limit during storage. The properties of testing clays including Rokaku, Ashikari and Okawa and two quick clays from Canada and Japan are tabulated in Table 1 for comparison. After storage, Rokkaku kawa, Ashikari and Okawa clays for 1 year, 3 months and 1.5 months, respectively, the liquid of all clays are decreased.

Location	Depth, m	Water Content , %	Liquid Limit, %	Plastic Limit, %	Specific Gravity	рН	Salt Content, g/l	Particle size distribution, %			Primary
								Sand	Silt	Clay	mineral
Ashikari	1.5-2.5	146.1	122.0	56.9	2.58	8.9	3.0	2.4	27.6	70.4	-
Rokkaku	0.5-1.0	123.2	141.6	54.1	2.56	7.6	4.4	2.1	29.9	68.0	-
Okawa	3.0-3.5	103.1	85.1	41.0	2.56	8.0	0.6	12.2	50.5	37.3	-
Quick clay (Canada) ¹⁾	10.0-10.5	45.0	25.0	20.0	2.75	9.5	-	0.0	48.0	52.0	Plagioclase
Quick clay (Yama-ashi) ²⁾	15.2-15.3	87	54.0	31.0	-	-	0.1	-	-	39.6	Non- swelling Smectite

Table 1 Properties of soil samples

Note: 1) Data from Lessard and Mitchell (1985) and sensitivity > 500. 2) Data from Egashira and Ohtsubo (1982) and sensitivity = 650.

As stated by Mitchell (1993), increasing in cation valence decreases the liquid value of expansive soil, but trends to increase the liquid limit of non-expansive soil. For expansive soil, the double layer is large can absorbed a lot of water. However, when the cations are added, the double layer thickness will decrease, therefore liquid limit decrease. For the non-expansive soil, when the cations are added, it will decrease of interparticle forces, increasing in liquid limit. In the quick clays, the one of primary factor required to developing quick clay is the domination of soil material mineral have to be non-expansive (Torrance and Ohtsubo, 1995). Due to this reason, the differences of liquid limit can possibly exist during oxidation process because of the difference in clay minerals. Anyhow, the mineral of the testing soil shall be further investigated to proof this assumption.

References IV

- 1. Egashira K. and Ohtsubo, M. (1982) "Smectite in marine quick-clays", Clay and Clay Mineral, vol. 30, No. 4, pp. 275-280.
- 2. Lissard, G and Mitchell, J. K. (1985) "The causes and effects of aging in quick clays", Canadian. Geotechnical Journal, vol. 22, pp. 335-346..
- Mitchell, J. K. (1993) *Fundamental of soil behavior*, 2nd ed. John Wiley & Sons, 437p.
 Soil experiment method (1969) "Soil experiment method", *Geotechnical Engineering Society* (in Japanese).
- 5. Torrance, J. K. (1976), "Pore water extraction and the effect of sample storage on pore water chemistry of Leda clay, Soil specimen preparation for laboratory testing", American Society for Testing and Materials, Special Technical Publication, No. 599, pp. 147-157.
- 6. Torrance, J. K. and Ohtsubo, M. (1995), "Ariake bay quick clays: comparison with the general model", Soil and Foundations, vol. 35, No. 1, pp. 11-19.