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SOLIDIFING SOIL AT ROOM TEMPERATURE WITH INORGANIC BINDER

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Solidifying soil at room temperature called as Tataki works was commonly used in bank protections and foundations, and are still functioning, during the past century in Japan. Using the weathered granite, small amounts of $Ca(OH)_2$ and water, Tataki works is mainly toughened with the carbonation at room temperature. Tataki works will be a solution of energy and resource-saving problem. In the present work, the influence of the aluminum and chlorine ions on the compressive strength of solidified body, *Tataki Work,* was evaluated. Both of the aluminum and chlorine ions increase toughening of compressive strength. The maximum compressive strength of 22MPa was obtained from the specimen with the 5% of $Al(OH)_3$ and 3% of 17.5%-bittern solution, curing for 28 days at 25℃, 80RH%. Calcium aluminum chloride hydrate called as Freedel's salt was formed when $Al(OH)_3$ and/or bittern were added, and its formation seemed to influence on the compressive strength.

Key words: solidifing soil, aluminum hydrate, chloride, Friedel's salt, calcite, compressive strength

1. INTRODUCTION

In recent years, due to global environmental problem, the realization of natural resource and energy saving type manufacturing technology has become a serious concern. In Japan, the "TATAKI" works, a solidification technology of soil at room temperature, have been used since long ago. Using the weathered granite (WG) with small amount of $Ca(OH)_2$ and water as the starting materials, solidification proceeds mainly with the carbonation of $Ca(OH)_2$. The TATAKI works can be described as an extremely small resource and energy required manufacturing technology where there is no use of specific resource and consumption of considerable energy. The TATAKI works have been traditionally applied to foundation, pavement around a house or well, however, in the early 20th century, it also applied to the civil engineering field such as seawall, bank protection and sluice gate. These TATAKI works have been functioning over the century and this indicates the possibility of higher durability.

Iizuka had reported manufacturing method of traditional TATAKI works.[1)] In the report, several factors to develop strength of Tataki works were described. However, the detailed mechanism of strengthen in the TATAKI works were neither clearly investigated in the previous report.

According to the authors, the first evaluation of the solidification mechanism in TATAKI works has been conducted. Through the current evaluation of TATAKI works constructed nearly 100 years ago,[2)] the authors researched that the development of strength was controlled by the carbonation of $Ca(OH)_2$ and the pozzolanic reaction related to calcium, aluminum and silicon elements. In addition, acceleration of carbonation coincides with formation of calcium aluminum chloride hydrate which is called as Friedel's salt when bittern was added, and their reaction seemed to influence on the compressive strength at the early stage.[3,4)]

Getting the further enhancement of the strength, the activator of solidifying reaction must be studied. Although there is no quantitative result about relationship between strength and Friedel's salt, previous conclusions imply that high enough aluminum coexisted with chlorine in the TATAKI specimen should facilitates to form Friedel's salt and causes to increase the strength. In this paper, the influence of Friedel's salt formation on the compressive strength of the TATAKI works is evaluated by adding $Al(OH)_3$ on the WG-$Ca(OH)_2$-bittern mixture.

2. EXPERIMENTAL PROCEDURE

The starting mixtures used were 87 mass % WG (from Nagiso in Japan, moisture content of 4 mass%, Table I, II), 10 mass% $Ca(OH)_2$ (Uedasekkai, Japan, industrial grade), and 3 mass% solution, such as water (named as N) or 17.5%-bittern ($MgCl_2 \cdot 6H_2O$, industrial grade) aqueous solution(named as C). In addition, the starting mixtures which were 82 mass% WG, 10 mass% $Ca(OH)_2$, 5 mass% $Al(OH)_3$ (Showa denko, Japan, H-43 grade) and 3 mass% 17.5%-bittern aqueous solution (named as AC) were used. Table III lists the mixing ratio of the three TATAKI preparations. The test specimens having the size of $40 \times 160 \times 20mm^3$ were formed by uniaxial pressing (30MPa) and cured at 25°C under 80%R.H. for 7 and 28 days.

Table I. Chemical Composition of Weathered Granite

elements	mass%
SiO_2	75.1
Al_2O_3	13.1
Fe_2O_3	2.0
CaO	0.9
MgO	0.2
K_2O	4.5
Na_2O	2.4
TiO_2	0.2
L.O.I.#	1.4

Loss on ignition

Table II. Mineral assemblage and median particle diameter

Mineral assemblage	Median particle Diameter (mm)
Quartz > orthoclase > albite > clinochlore > muscovite > kaolinite	1.18

Table III. Mixing ratio of the TATAKI preperations

Specimen	N	C	AC
Weathered granite	87	87	82
$Ca(OH)_2$	10	10	10
$Al(OH)_3$	---	---	5
water	3	---	---
17.5%bittren solution	---	3	3

unit : mass%

After curing, the compressive strength of the specimens was measured (CATY-3005, YONEKURA MFG. Co., Ltd., Japan, cross-head speed 0.1mm/min, no. of 3 specimens). Phases were identified by XRD analysis (RAD-B, Rigaku, Japan) and thermogravimetric (TG) analysis (TSA300, Rigaku, Japan) up to 1100°C, with a heating rate of 20°C$\cdot$min^{-1} in N_2 gas flow.

3. RESULTS

3.1 Strength

Figure 1 shows that the specimen AC which includes $Al(OH)_3$ and bittern solution gave the maximum compressive strength of 22MPa, contrasting the specimen N 9MPa, specimen C 13MPa, after 28 days curing. It was clear that the addition of Al (OH) 3 and chloride increased the compressive strength.

After 7 days curing, the compressive strength also tended to rise with addition of $Al(OH)_3$ and bittern solution. It is consequently expected that an enhancement of the strength in the early stage of the solidification is obtained where the both of $Al(OH)_3$ and chloride solution are added.

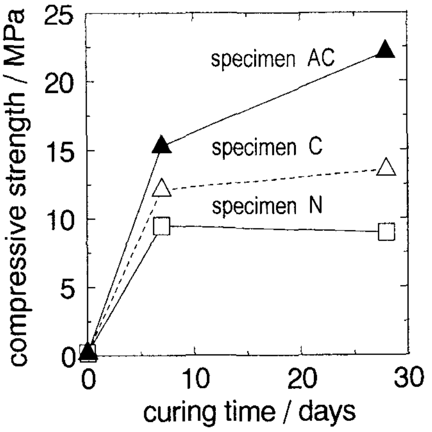

Figure 1 Compressive strength of the three TATAKI specimens.

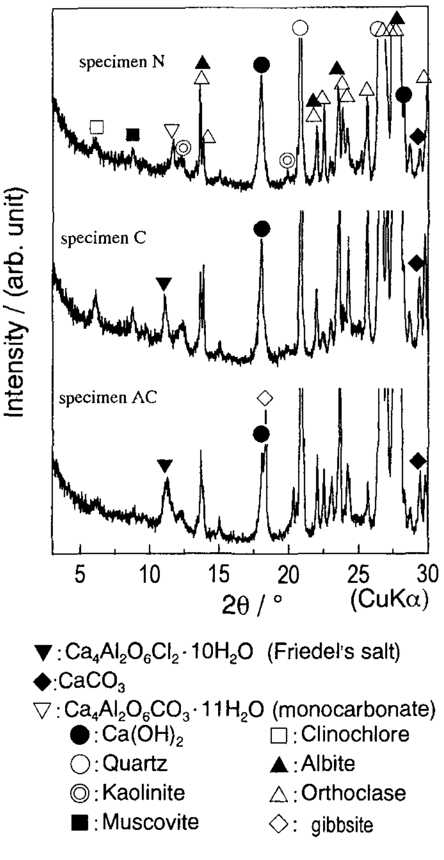

Figure 2 XRD pattern of the three TATAKI specimens.

3.2 Phases Formed

Figure 2 shows the XRD patterns for the specimens cured for 7 days. Formation of calcite ($CaCO_3$) was observed in all specimens. The peak intensities of calcite for the specimens mixed with chloride solutions were higher than the specimens with no addition.

In the specimens AC and C which were mixed with chloride, the formation of Friedel's salt ($Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O$) was observed. This salt was not observed in the specimens without addition of chloride. The peak intensity of Freidel's salt for the specimen AC was higher than the specimen C. Calcium aluminum monocarbonate hydrate ($Ca_3Al_2O_6 \cdot CaCO_3 \cdot 11H_2O$) was observed in the specimen N.

TG traces among the three TATAKI specimens cured for 28 days exhibit decomposition behavior of the phases formed. The weight losses due to phase transition of calcium aluminum hydrate appeared around 200℃ for all the three specimens.[5] Decomposition of $CaCO_3$ also appeared in the three specimens between 500 and 700℃. The weight loss caused by de-hydration of $Ca(OH)_2$ was observed around 450 ℃. In the specimen AC, de-hydration of $Al(OH)_3$ was observed around 270℃. Total weight losses of the specimens AC, C and N were 8.3, 6.3 and 5.2%, respectively.

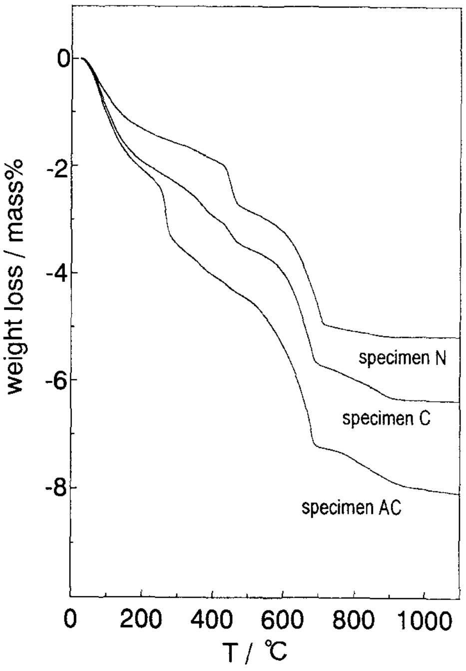

Figure 3 TG traces of the three TATAKI specimens.

4. DISCUSSION

The TG analysis suggests that the specimen AC should have the largest quantity of the reaction products in the three specimens, because of maximum weight loss. In this paper, quantities of Friedel's salt and $CaCO_3$ formed in the three specimens are evaluated from the decomposition behavior between 40 and 700 ℃. Therewith, influence of the phases formed on the compressive strength is discussed.

4.1 Quantitative Comparison of Friedel's Salt

Ahmed et al. had discussed that the thermal decomposition of $Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O$ was distinguished into three steps which occur 40-170℃, 290-380℃ and 740-880℃, respectively.[5] The author focuses on the first step of the reaction to quantify Friedel's salt, since the first transformation of Friedel's salt seems to release the largest amount of water molecules in the three steps.

At the temperatures 40-170℃, weight losses of the specimens AC, C and N were 1.8, 1.5 and 1.1%, respectively. Assuming the reaction; $Ca_3Al \cdot CaCl_2 \cdot 10H_2O \rightarrow Ca_3Al \cdot CaCl_2 \cdot 6H_2O + 4H_2O \uparrow$ occurs in the temperature range, quantities of Friedel's salt can be calculated to 13.3% for the specimen AC and 11.1% for the specimen C. The calculation result indicates that quantity of Friedel's salt formed in the former is about 1.2 times larger than that in the latter. However, a phase formed in the specimen N can not be quantified as decomposition reaction is not clearly identified. Calcium aluminum monocarbonate hydrate may become an amorphous phase.[6]

4.2 Quantitative Comparison of Calcite

As shown in Fig. 3, decomposition of calcite, $CaCO_3 \rightarrow CaO + CO_2 \uparrow$, was observed in the three specimens at 500-700 ℃. Weight losses of the specimens AC, C and N were 2.9, 2.2 and 1.9%, respectively. From those weight losses, quantities of $CaCO_3$ can be calculated to 6.6% for the specimen AC, 5.0% for the specimen C and 4.3% for the specimen N. This result indicates that $CaCO_3$ formed in the specimen AC is observed about 1.3 times larger than that of the specimen C, and is about 1.5 times larger than that of the specimen N.

Assuming Friedel's salt and $CaCO_3$ were produced from $Ca(OH)_2$, approximately 12% of $Ca(OH)_2$ must be required to form 13.3% Friedel's salt and 6.6% $CaCO_3$ in the specimen AC which was mixed with $Al(OH)_3$ and chloride solution. The reason why the error of 2% $Ca(OH)_2$ was represented is that weight loss measurement includes an error due to adsorbed water and/or heterogeneity of the specimens. Another reason can be considered that Friedel's salt formed in the specimens included non-stoichiometric and/or amorphous phases as the XRD peak of (001) seems to broad shape.

4.3 Influence of Phases Formed on Strength

Results indicate that the addition of $Al(OH)_3$ and chloride accelerate the formation of Friedel's salt and $CaCO_3$, hence, the compressive strength increased. The behavior that the compressive strength tended to rise with the increasing of the phases formed, can be considered due to rapidly microstructure development in the TATAKI preparation under the presence of highly concentrated aluminum ions coexisted with chlorine ions. However, it is not differentiated that influence of the phases formed; Friedel's salt and $CaCO_3$, on the strength of the TATAKI works,

Regarding the influence of Friedel's salt, Suryavaushi et al. reported that the Friedel's salt, whose formation was recognized in the specimen with addition of chloride, was easily formed in the hydration of cement with chlorine ion and worked as a strength developing factor.7,8) On the other hand, it was also confirmed that the Friedel's salt had relatively low density9) and showed the internal stress in concrete.10) This may indicate the fact that Friedel's salt precipitates rapidly and fills micro pores in the TATAKI specimen.

In consequently, although it is not clear that how the formation of Friedel's salt affects directly to the strength, Friedel's salt acts as a binder and a filler materials, and increases the strength at early stage of the solidification.

5. CONCLUSIONS

1) The compressive strength was increased by the addition of $Al(OH)_3$ and chloride solutions. The maximum compressive strength of 22MPa was obtained from the specimen mixed with 5 mass% $Al(OH)_3$ and 3% 17.5%-bittern solution, cured at 25°C under 80%R.H. for 28 days (9MPa without addition of $Al(OH)_3$ and chloride).

2) Friedel's salt and $CaCO_3$ formed in the TATAKI specimens were quantified by calculation of TG analysis results. Friedel's salt were calculated to 13.3% for the specimen mixed with $Al(OH)_3$ and chloride solution, 11.1% for the specimen mixed with chloride solution. Calcite formed was quantified to 6.6% for the specimen mixed with $Al(OH)_3$ and chloride solution, 5.0% for the specimen mixed with chloride solution and 4.3% for the specimen with no addition.

3) By the addition of both $Al(OH)_3$ and chloride, the formation of Friedel's salt and $CaCO_3$ were accelerated, hence, the compressive strength increased. Although it is not clear that how the formation of Friedel's salt affects directly to the strength, Friedel's salt acts as a binder and a filler materials, and increases the strength at early stage of the solidification.

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