

Research on soil solidification treatment using waste oyster shells

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ABSTRACT

Social concern for environmental preservation and resource recycling has been increasing, the ground improvement with less environmental impact should be desired. This study experimentally investigated the effective use of oyster shells, an industrial waste, and the use of phosphoric acid for soil cementation. Batch tests were conducted to find the optimum conditions for the cementation process. The results of pH, EC, and Ca^{2+} measurements of the phosphoric acid solution after curing indicated that the solution with 200 times dilution by water was the most suitable. Column tests were conducted to examine the effect of sample column anisotropy on strength. Unconfined compression tests of the specimens were performed, and the specimens were observed with a scanning electron microscope. From these results, it was confirmed that the specimens produced by the improved curing method were approximately four times stronger than those before the improvement.

RÉSUMÉ

La préoccupation sociale pour la préservation de l'environnement et le recyclage des ressources a augmenté, et il en va de même pour l'amélioration des sols. Cette étude a examiné expérimentalement l'utilisation efficace des coquilles d'huîtres, un déchet industriel, et l'utilisation de l'acide phosphorique pour la solidification du sol.

Des tests par lots ont été réalisés afin de trouver les conditions optimales pour le processus de solidification. Les résultats des mesures de pH, EC et Ca^{2+} de la solution d'acide phosphorique après la solidification ont indiqué qu'une solution aqueuse d'acide phosphorique avec un facteur de dilution de 200 était la plus appropriée.

Des essais sur colonne ont été effectués pour examiner l'effet de l'anisotropie de la colonne de l'échantillon sur la résistance. Des essais de compression uniaxiale des échantillons ont été réalisés, et les échantillons ont été observés avec un microscope électronique à balayage. D'après ces résultats, il a été confirmé que les spécimens produits par la méthode de durcissement améliorée étaient environ quatre fois plus résistants que ceux avant l'amélioration.

Key Words: Oyster shells, Calcium phosphate compounds, Cementation treatment

1 INTRODUCTION

Currently, the grout method using artificial materials such as cement and water glass are common techniques for improving the mechanical and hydrodynamic properties of the ground. Although improvements using cement are widely and commonly used, they are known to affect the surrounding ground environment. Social interests such as environmental conservation and resource recycling have become increasingly important in various fields, and the field of geotechnical engineering, there is a growing demand for ground improvement technology that makes effective use of resources and uses new materials with less environmental impact.

In this study, the oyster shells are used, which are disposed of as waste from an oyster farm in Rikuzentakata City, Iwate Prefecture, Japan. The tsunami caused by the Pacific coast of east Japan earthquake reduced the oyster harvest in Iwate Prefecture from 9,578 t in 2010 to 565 t in 2012. According to the Ministry of Agriculture, Forestry and Fisheries (2021), the harvest has steadily increased year by year since then, recovering to 6,341 t in 2019, about 70% of the pre-earthquake harvest. With the increase in harvest volume, the amount of oyster shells discarded has also increased.

In recent years, various studies on the effective use of shells have been reported in the field of civil engineering.

The previous studies are following. Yamauchi et al. (2005) examined the workability and durability of concrete using crushed scallop shells as fine aggregate, and showed that it is comparable to ordinary concrete. Yamada et al. (2005) confirmed the effects of using crushed oyster shells in combination with stabilizers to neutralize acid sulfate soils, increase bearing capacity, and reduce the amount of stabilizer. Yamagishi et al. (2007) showed that the slip resistance of road surface marking paints with crushed scallop shells as an additive was superior to that of currently used additives. Miyaji et al. (2010) examined the practical feasibility of using scallop shells as a filtering material for wastewater purification. Shigematsu et al. (2012) experimentally investigated the effect of ground surface materials mixed with scallop and oyster shells on soil compaction, bearing capacity, and permeability. Kanayama et al. (2013) experimentally examined microbial cementation treatment of soil using oyster shells due to the metabolic activity of microorganisms, and confirmed that the deposited calcium carbonate increased the strength of soil samples.

Research on calcium phosphate compounds has been conducted mainly in medicine and dentistry (Ginebra et al., 2006; Bohner et al., 2006), but they are still in the research

stage in agriculture and geotechnical engineering (Akiyama & Kawasaki, 2011), and are expected to attract more attention in the future. In this study, basic laboratory tests using oyster shells were conducted to evaluate the cementation performance of calcium phosphate compounds.

The purpose of this study is to develop a new soil cementation method and to propose an effective way to utilize oyster shells. Oyster shells, an industrial waste, were used as a new material with less environmental impact, and the soil cementation process was investigated experimentally.

In this study, optimal conditions for strength increase and homogenization were investigated by conducting batch tests. The specimens were tested for homogenization of the manufactured specimens based on the results of the batch tests in column tests, and the micro-region chemistry was characterized using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

2 MATERIALS AND TEST METHODS

Oyster shells were obtained from the oyster shelling facility at Ryogae Fishing Port in Rikuzentakata City, Iwate Prefecture, and were piled in the field for at least one year. The shells were roughly crushed with a hammer and sieved to obtain a uniform particle size: 2000-475 μm , 425-200 μm , 75-425 μm , and 75 μm or smaller. In batch test, the specimens with 425-2000 μm and 75-425 μm particle sizes were used. In column test, the specimens with 425-2000 μm particle size was used.

Phosphoric acid was a special grade reagent from Hayashi Pure Chemical Industry Co. This phosphoric acid has a density of approximately 1.69 mg/L (85%) at 20 °C. Because of its high concentration and environmental impact, it was diluted with distilled water to the desired ratio and used as an aqueous phosphoric acid solution.

Toyoura standard sand was used as the sample for the column test because it has uniform grain size and is high reproducibility in the experiment. The physical properties of Toyoura standard sand are shown in Table 1.

To solidify soil was focused on calcium phosphate compounds, which are the main constituents of bones and teeth among natural substances. Calcium phosphate compounds are precipitated by the reaction of calcium carbonate, the main component of oyster shells, and phosphoric acid, which produces carbon dioxide (hereinafter referred to as CO_2) and water as byproducts. Below is a simple chemical reaction equation [1] for calcium carbonate and phosphoric acid.



2.1 Batch test

Oyster shells were crushed to a defined particle size for the sample. The test conditions are shown in Table 2. One gram of oyster shell was placed in a 60 ml test tube with a dispensing spoon, and 20 ml of phosphoric acid solution of a given concentration was injected into the test tube. The

test tubes were then placed on a test tube stand and allowed to leave until the specified curing time.

The tests performed in the batch tests were: 1) curing of the specimens in test tubes, 2) measurement of pH, Ca^{2+} concentration, and electrical conductivity (EC) of the phosphoric acid solution used for curing (Horiba, LAQUAtwin, B-71X, B-751, B-771), and 3) observation of the structural skeleton of the specimens using a scanning electron microscope (SEM) and energy distributed X-ray spectroscopy (EDS). The structural skeleton was observed using a scanning electron microscope (SEM), which can observe structures down to the nanometer level. Image observation was conducted to obtain detailed information on the structure of dissolved oyster shells and precipitated calcium phosphate compounds, as well as the distribution area and mass ratio of sand, oyster shells, and calcium phosphate compounds. Before observation, osmium was deposited on the specimens to prevent charging of the specimens. The plasma coater for osmium was OPC40 and the scanning electron microscope was a JSM-7800F PRIME.

2.2 Column test

The sample was a mixture of Toyoura standard sand and oyster shells in a specified ratio. Oyster shells passed through a 2000 μm sieve and remained on a 425 μm sieve. The samples were packed in a column, and phosphoric acid solution was pumped through the column. The test conditions are shown in Table 2, and the column test is shown in Figure 1. The solution was changed once a day, during the curing period. The tests conducted in this study were: 1) curing of the specimens in columns, 2)

Table 1. Physical properties of Toyoura standard sand

Soil particle density ρ_s (g/cm^3)	2.64
Minimum soil particle density $\rho_{d \text{ min}}$ (g/cm^3)	1.335±0.005
Maximum soil particle density $\rho_{d \text{ max}}$ (g/cm^3)	1.645±0.010
Maximum void ratio e_{max}	0.973
Minimum void ratio e_{min}	0.609
Average particle diameter D_{50} (mm)	0.17
10% particle diameter (mm)	0.17
Fine fraction content F_c (%)	0

Table 2. Test name of batch test

Test name	Phosphoric acid aqueous solution dilution ratio	Particle size (μm)	Curing period (h)
a	50	425~2000	1, 2, 4,
b		75~425	6, 24
c	100	425~2000	
d		75~425	
e	200	425~2000	
f		75~425	
g	400	425~2000	
h		75~425	
i	800	425~2000	
j		75~425	

measurement of pH, Ca^{2+} concentration, and electrical conductivity (EC) of the phosphoric acid solution used for curing, 3) evaluation of strength constants of the specimens cured in column tests by uniaxial compression tests (target strength: 100 kN/m^2), and 4) observation of the structural framework of the specimens using SEM and EDS.

A cylindrical column with a diameter of 4.5 cm and a height of 8.5 cm was used for the column test in 1). Tubes were connected to the both sides, and phosphoric acid solution was injected from the side of the column to another side using a feed pump. The injected aqueous phosphoric acid solution was not circulated, but was left to react for 24 hours. The test condition is shown in Table 3.

To confirm the progress of the reaction between phosphoric acid and oyster shell in (2), the pH, calcium ion concentration, and EC of the phosphoric acid solution taken out at a specified frequency were measured. Phosphoric acid solutions taken from solution columns were measured every few hours with a compact ion meter (similar to the batch test), except when the pH was too low or the calcium ion concentration was too high in OyS1, in which case the solution was basically replaced by the aqueous phosphoric acid solution. The exchange of the two types of products was decided. Phosphoric solution was not replaced only on the 11th day of curing when pH reached the 3 level and on the 13th day of curing when calcium ion concentration exceeded 650 mg/L . In OyS2, phosphoric solution was replaced daily.

The uniaxial compressive strength, q_u (kN/m^2), which is an index for the actual treatment as a ground

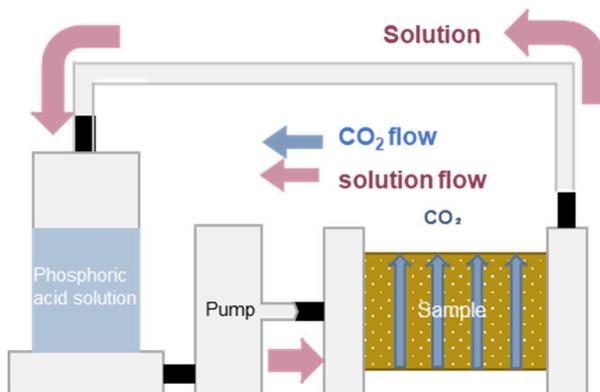


Figure 1. Test method of column test

Table 3. Test condition of column test

Test name	OyS1	OyS2
Mixture ratio (Soil to Oyster shell)	1 to 0.3, 1 to 0.5	1 to 1, 1 to 0.75
Phosphoric acid solution dilution ratio	100	200
Solution exchange frequency	Depends on the measured value	Everyday
Curing period (day)	14	28
Flow direction	Horizontal	Vertical, Horizontal

improvement material in the field, was evaluated by uniaxial compression tests of the specimens solidified in the column test. The target uniaxial compressive strength of the specimens was set to $q_u = 100 \text{ kN/m}^2$, which can be used for soil improvement of soft soils, and the specimens were compressed at a compressive strain rate of $1\%/min$. Uniaxial compression tests of the specimens were performed in a laboratory using a universal compression testing machine (A&D Corporation, RTG-1210) and general-purpose testing machine data processing software (TACT: Tension Advanced Controller for Testing).

3 RESULTS AND DISCUSSION

3.1 Batch test

Batch tests were conducted in test tubes to determine the optimum conditions for the concentration of phosphoric acid solution and the optimum conditions for particle size.

Figure 2 shows the condition during curing. In the test tubes with particle diameters between 75 and $425 \mu\text{m}$, the phosphoric acid solution reacted with oyster shells when injected, producing a large amount of CO_2 that overflowed the test tubes. The effluence of the solution was not observed in the case of oyster shells with particle sizes of $425 \mu\text{m}$ to $2000 \mu\text{m}$.

This is thought to be due to the fact that the smaller the particle size, the larger the specific surface area. This reaction tends to be stronger as the concentration of the phosphoric acid solution increased. The cementation reaction proceeds slower when the particle size of oyster shells is larger and the concentration of aqueous phosphoric acid solution is lower.

Various measurements of pH, electrical conductivity (EC) and Ca^{2+} concentration of the phosphoric acid solution used for curing are shown in Figure 3. The pH of the aqueous phosphoric solution in the test tubes after 24 hours of curing exceeded 6.0 except for the test condition a. This is because the aqueous phosphoric acid solution reacted and turned into water, while, in the test condition a, the calcium phosphate compounds could not be precipitated under high acidic condition. Therefore, a phosphoric solution with 50 times dilution by water is not

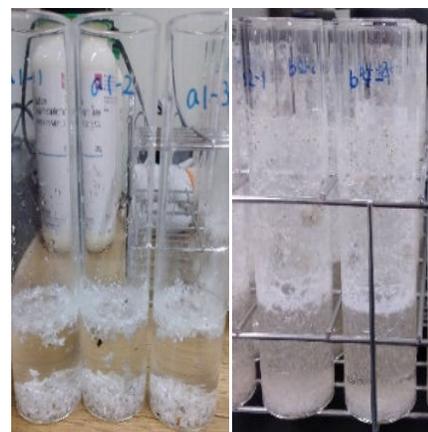


Figure 2. Test tubes during curing of a, b

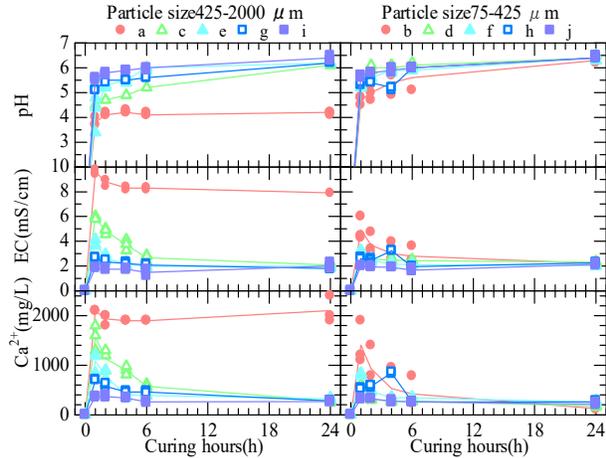


Figure 3. Various measurements of batch test

suitable for cementation because calcium phosphate compounds (hereinafter referred to as precipitates) are also dissolved out of the solution.

According to the behavior of Ca^{2+} values, the amount of the precipitates were considered to the amount of the decreases in the Ca^{2+} values. Under test conditions b, c, d, e, and f, Ca^{2+} reaches above 1000 mg/l and then below 300 mg/l. Therefore, it is considered that more precipitates are deposited in aqueous phosphoric acid solutions at 100 and 200 times dilution by water than in other test conditions. From previous studies, it is suggested that the reaction proceeds more slowly and the homogeneous specimens can be produced when aqueous phosphoric acid solutions are diluted as much as possible. These results indicate that an aqueous phosphoric acid solution with 200 times dilution by water is most suitable.

After 24 hours of curing, the specimens were oven-dried, and images observed by SEM are shown in Figure 4. The upper left is the SEM image of oyster shell with grain size of 75-425 μm , and the lower left is the result of its EDS elemental analysis. The SEM and EDS images of oyster shells with grain sizes ranging from 425 to 2000 μm are shown on the right. For the precipitates of 75 to 425 μm specimen, as the size was about 1 μm , the relatively small particle structure was formed. On the other hand, 425 to 2000 μm , the size was ranged from 100 to 200 μm . From EDS analysis, the calcium phosphate compounds were detected in all test conditions. These results suggest that oyster shells with particle sizes between 425 and 2000 μm complicate the structure within the sample, while oyster shells with particle sizes between 75 and 425 μm fill the pore spaces. (Figure 5)

3.2 Column test

For the column test, the effects of the dilution ratio in the solution and the mixture mass ratio between sand and oyster shell were examined. In OyS1, the concentration of phosphoric acid solution was set to 100 times dilution by water, and the effect of the dilution ratio on the cementation was observed in comparison with OyS2. The adopted mixture mass ratios were 1: 0.3 and 1: 0.5 (sand: oyster

shell) on the strength of specimen. The sample column was placed horizontally and cured.

The results of various measurements of OyS1 are shown in Figure 6. When 24 hours passed after the change of the phosphoric acid solution, the pH values were ranged from about 4.0 to 6.0. In all specimens the pH showed the order of 5 and the average was 5.4. The pH did not reach a value near neutral. This is thought to be due to the fact that the reaction with the oyster shells and the phosphoric acid solution occurred locally because the solution is not circulated. The relatively low pH value implies the high concentration of phosphoric acid solution, and this means that phosphoric ions remain in the solution without fully reacting with the oyster shells.

According to the EC measurement, the EC values varied 1.32 to 6.59 mS/cm. After injecting the solution to the column, the value showed high and then after 24 hours the values decreased about a half. The trend was observed until 14 days, suggesting that the productive reaction of calcium phosphate compounds occurred in these time range. Similar changes were observed for different proportions of oyster shells, and no differences were found in the individual measurements.

The calcium ion concentrations immediately after the phosphoric acid solution was injected the first day were high, ranging from 530 to 820 mg/L. On the other hand, calcium ion concentrations on subsequent days when the solution was changed were low, ranging from 15 to 320 mg/L. After the solution was injected on the first day, the Ca^{2+} concentrations were high, with an increase of curing time, the Ca^{2+} concentrations were low. The decline of the

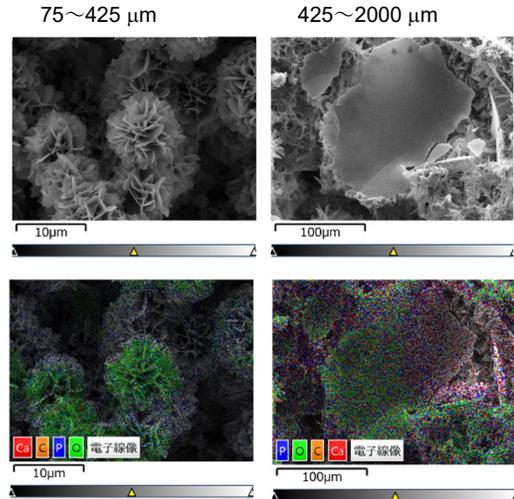


Figure 4. Image of SEM, EDS

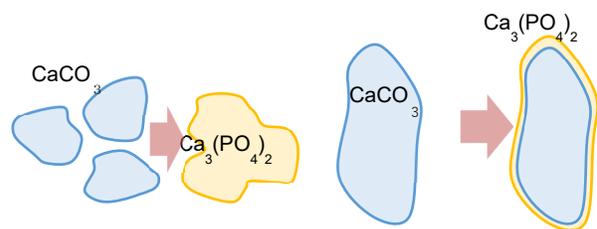


Fig.5 Structure model

Ca²⁺ concentration is considered to be either the consumption by chemical reaction or the mixture with the solution before and after the reaction.

In test condition OyS2, the effect of anisotropy on the strength of specimen was examined. The dilution by water was 200 times and the adopted mixture mass ratio were 1:0.75 and 1:1 (sand: oyster). The effect of anisotropy of curing on the strength of the sample columns was examined by using vertical curing and horizontal curing.

Figure 7 shows the results of various measurements on OyS2. In all cases, the variation of the measurements showed the same trend until 28 days curing period. This indicates that the reaction to precipitation of calcium phosphate compounds continued to progress during curing. It is believed that the reaction proceeds slowly because the concentration of the phosphoric acid solution was diluted less than the 100-fold dilution used in the previous study.

The results of the uniaxial compression test of OyS1 are shown in Figure 8 as a stress-strain curve. For the samples with the mixture ratio, 1: 0.3 and 1: 0.5, with an increase of curing time, the maximum compressive strength increased from 18.8 to 29.3, from 34.3 to 53.5 kN/m², respectively. The strength of the 0.5 oyster shell specimens was greater

than that of the 0.3 oyster shell specimens. The more oyster shells are used, the more calcium phosphate compounds precipitate and the higher the strength of the material. The strength of the 14-day cured specimens was greater than that of the 7-day cured specimens.

The results of uniaxial compression tests of OyS2 are shown in Figure 9. According to the OyS2 test conditions, horizontal curing resulted in higher uniaxial compressive strength than vertical curing, 39.0 and 7.9 kN/m² at a mix ratio of 1:0.75 and 64.2 and 23.7 kN/m² at 1:1, respectively. Under test condition OyS2, the phosphoric acid solution was diluted 200 times and cured for a longer period to dissolve the oyster shells little by little while cementation proceeded. This is thought to have made the specimens homogeneous. Compared by curing method, the specimens with horizontal curing had higher strength and stiffness. In horizontal curing, the contact area between the phosphoric acid solution and the sample is larger than that of vertical curing, and curing proceeds over a wider area. As a result, it is considered that the cementation is homogeneously cured and the stiffness is increased.

Comparing the results of OyS1 and OyS2, the highest uniaxial compressive strength and stiffness were obtained for the specimens cured horizontally with a 1 to 1 oyster shell to sand ratio. This suggests that the ratio of oyster shells and the anisotropy of the curing process affect the

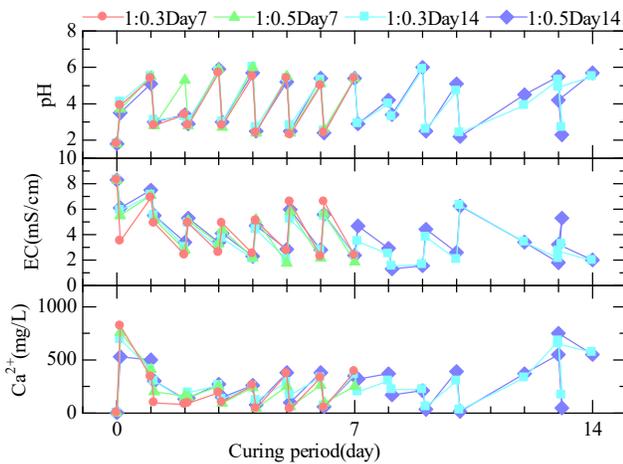


Figure.6 Various measurements of OyS1

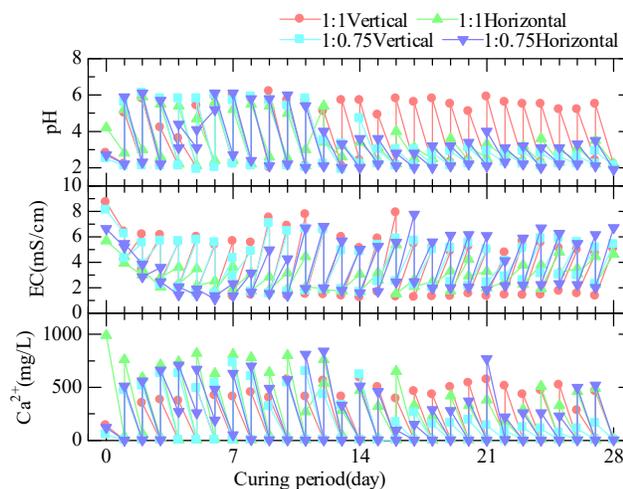


Figure 7. Various measurements of OyS2

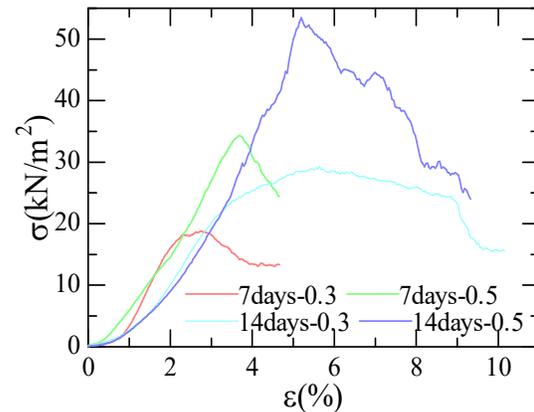


Figure 8. UC test result of OyS1

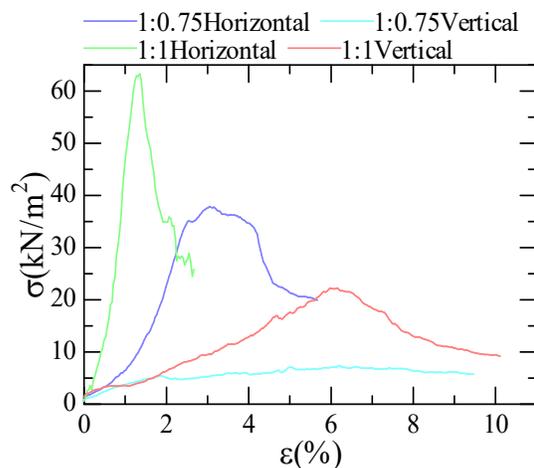


Figure 9. UC test result of OyS2

strength increase. The high composition ratio is thought to have contributed to the increase in strength through the formation of a large number of precipitates and the filling of pores.

Figure 10 shows SEM and EDS images of Oys2. The upper left image is the SEM image of the specimen cured vertically at a ratio of 1:0.75, and the upper right is the EDS image of the specimen. Similarly, the under two images are SEM and EDS images of a specimen cured horizontally at a ratio of 1:1. The SEM images show that the specimen with a higher ratio of oyster shells has fewer pores, and the particles are bound together to form a large mass. The EDS results showed that calcium phosphate compounds were precipitated in the areas where phosphoric acid elements were observed, which filled the pore spaces. As predicted in the batch tests, oyster shells complicated the structure within the sample, entrapping soil particles and filling the pore spaces between them. In addition, calcium phosphate compounds were found to precipitate over the soil particles. These are thought to connect the soil particles and contribute to the increase in strength. Above description was shown in the Figure 11.

4 CONCLUSION

In this study, a new soil cementation process was developed, and an effective use of oyster shells was proposed. The insights obtained in this study are as follows.

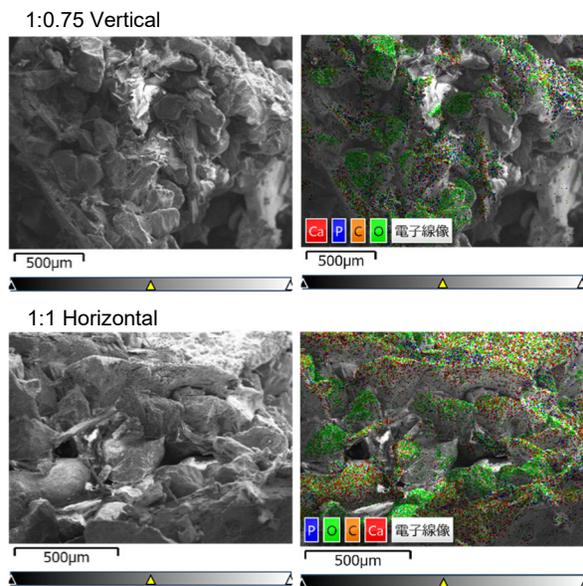


Figure 10. SEM, EDS results

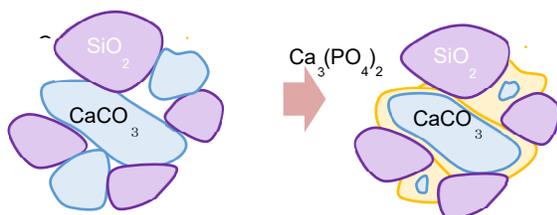


Figure 11. Structure model

(1) From the batch test results, it was found that the optimum of the phosphoric acid solution was 200 times dilution by water.

(2) Regarding particle size, it was shown that it is preferable to use a mixture of medium and small particles or only medium particles because the smaller particles have a larger specific surface area, and the reaction proceeds faster.

(3) In the column test, the results of various measurements showed that the stiffness increased for the test with a of 200 times dilution by water due to the continuous progress of the reaction.

Uniaxial compressive strength increased with increasing oyster shell content.

(4) In column tests, horizontal curing showed higher uniaxial compressive strength than vertical curing.

(5) SEM and EDS results indicate that the oyster shells complicated the structure within the sample, entrapping the soil particles and filling the pore spaces between them. In addition, calcium phosphate compounds were found to precipitate over the soil particles. It was confirmed that these factors connected the soil particles and contributed to the increase in strength.

(6) Uniaxial compression tests and the results of SEM and EDS indicate that calcium phosphate compounds contribute to the strength increase by precipitating in the pores.

In the future, we would like to accumulate more data and link the SEM and EDS results to uniaxial compressive strength to analyze the factors of strength increase and the structure of precipitation as more accurate data.

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