Improvement in the Unconfined Compressive Strength of Sand Test Pieces Cemented with Calcium Phosphate Compound by Addition of Calcium Carbonate Powders

G. G. N. N. Amarakoon¹,*, Takefumi Koreeda¹ and Satoru Kawasaki²

¹Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan
²Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Grouting using calcium phosphate compound (CPC) has been used for countermeasure for liquefaction in geotechnical engineering applications and it is an economical and environmental friendly technique that develops to form calcium carbonate precipitation throughout the soil, leading to an increase in soil strength. In the paper, our aim was to improve strength by adding CPC with CaCO₃ (commercially found) and scallop shell (Naturally found) powder and exceed a maximum UCS of 100 kPa after 28 days of curing, which is the strength required as a countermeasure against soil liquefaction during earthquake. For that, initially Toyoura sand test pieces were cemented by CPC solutions only and cured up to 56 days and carried out unconfined compressive strength (UCS) test. Moreover, Toyoura sand test pieces were cemented by CPCs with CaCO₃ (CC) powder and CPCs with scallop shell powder and cured and these specimens also analyzed with UCS tests. The UCS of the sand test pieces cemented by CPC with scallop shell powder and CC powder was higher than that of the test pieces with no added powders. In addition, a series of laboratory experiments were conducted, including pH concentration, scanning electron microscope (SEM) in order to observe the microscopic structure, density before and after curing etc. The results indicate that the density and the pH concentration of the sand test pieces cemented by CPC with scallop shell powder and CC powder were higher than that of the test pieces with no added powders.

Keywords: calcium carbonate, calcium phosphate compound, ground improvement, unconfined compressive strength

1. Introduction

Soil liquefaction describes a phenomenon whereby a saturated soil substantially loses strength and stiffness in response to an applied stress, usually earthquake shaking, causing it to behave like a liquid. The effects of liquefaction have been long understood, it was more thoroughly brought to the attention of engineers after the 1964 Niigata earthquake and 1964 Alaska earthquake. In Japan, many areas are potential to liquefaction after earthquake is happened. Therefore, there is an urgent need for countermeasures for soil liquefaction.

Cement grouting is commonly used for as a ground improvement method and it plays an important role as countermeasures against disasters, including ground liquefaction during an earthquake. However, cement grouting comprises quite a lot of environmental problems. Therefore in recent years, grout materials that abuse mechanisms of cement material production by microorganisms have been developed for ground permeability control and reinforcement.

The process of ground improvement by biological action is called “biogrouting”. For biogrouting, there are three mechanisms of mineral formation have to be considered: Precipitation of calcium carbonate by in situ microorganisms and/or added yeasts, precipitation using urea and ureolytic bacteria, and siloxane bond formation using glucose and yeast.

In recent years, a novel ground stabilizer developed to increase the number of options available among cementing mechanisms based on microorganisms. Further, it is reported on a CPC chemical grout (CPC-Chem) that utilizes self-setting CPC mechanisms (Fig. 1(a)), and on a CPC biogrout (CPC-Bio) whose solubility is dependent on its pH (Fig. 1(b)), which can be increased by a microbial reaction. CPC-Chem is easy to obtain, safe to handle, non-toxic, and recyclable, advantages that make it suitable for geotechnical
The maximum UCS of sand test pieces cemented with CPC-Chem was found to be 63.5 kPa. When CPC-Chem was converted to CPC-Bio by the addition of microorganisms and an ammonia source, the UCS increased from 42.9 to 57.6 kPa. Our aim was to achieve a UCS value of 100 kPa, which is needed to avoid ground liquefaction during earthquakes. This implies that the UCS of both CPC-Chem and CPC-Bio is not sufficient for use as a ground stabilizer, necessity of a preferable mechanism for further increase in UCS.

Research on CPC precipitation and solidification is also currently underway in the field of medical and dental science. A research on CPC paste has reported that the uncompressed compressive strength (UCS) of CPC exceeds 10 MPa under normal temperature and pressure conditions. In addition it has showed that the compressive strength of a mixture paste of dicalcium phosphate (DCP) and α-tricalcium phosphate (TCP) reached can be increase from 35 MPa to a maximum of 56 MPa by using calcium carbonate (CC) as the seed crystal. A previous research is said, the UCS of the test pieces with TCP and CC additives exceeded the targeted value of 100 kPa and increased to a maximum of 261.4 and 209.7 kPa respectively. This observations indicates that the existence of CC seed crystals can reinforce the strength of CPC grouts, such as the grout used in this study. CC is the main component of scallop shells, which are disposed of in large quantities as marine industrial waste (410,000 tons/year in Japan). Moreover, it is non-toxic to handle and inexpensive to obtain. Thus, CC is a promising material in the geotechnical field from the viewpoint of waste utilization and cost effectiveness.

In the present study, our aim was to improve strength by adding CPC with scallop shell powder. This study aims to exceed a maximum UCS of 100 kPa after 28 days of curing, which is the strength required to use the CPC and scallop shell powder combination as a countermeasure against soil liquefaction during earthquake. We carried out UCS tests and scanning electron microscopy (SEM) observations on sand test pieces as a function of time. Based on the results, we discuss the effect of the kind and amount of added powders and crystal form on the UCS.

2. Methodology

The CPC-Chems used in this study were 0.75 M : 1.5 M mixture of calcium acetate (CA) and diammonium phosphate (DAP); we used this mixture because it has previously been reported that this mixture yields the highest UCS among all combination ratios of DAP with calcium nitrate or CA, and 0.6 M : 1.2 M mixture of calcium acetate (CA) and dipotassium phosphate (DPP). Toyoura sand test pieces were cemented by CPCs with CaCO3 (CC) powder which was taken by commercially and CPCs with scallop shell (SS) powder and cured and these specimens also analyzed with UCS tests. Hereafter, CaCO3 powder is referred to as CC method and scallop shell powder is referred to as SS.

A standard sand test piece was made from 320.09 g of Toyoura sand (mean diameter \(D_{50}=170\ \mu m\), 15\% diameter \(D_{15}=150\ \mu m\)) and 73.3 mL of CPC-Chem according to the previous report, and the examined test pieces were made with the combination ratios and wet density shown in Fig. 2. \(1\%\) (3.2 g) (Case SS-01 and CC-01), 5\% (16.0 g) (Case SS-05 and CC-05), and 10\% (32.0 g) (Case SS-10 and CC-10) of CC (mean diameter \(D_{50}=14.52\ \mu m\)) and SS (mean diameter \(D_{50}=25.12\ \mu m\)) were mixed with 72.21, 67.84, and 62.38 mL of CPC-Chem respectively and added to weight of a standard sand test piece of 320.09 g. It was uniformly mixed in a stainless-steel ball for 2 min and the mixture was divided into quarters, each of which was placed into a plastic mold container (\(\phi=5\ cm,\ h=10\ cm\)). The sand in the mold container was tamped down 30 times by a hand rammer after each of the four quarters was placed in the mold. The molded test pieces were subsequently cured in an airtight container at a high humidity for 56 days at 20°C.

The control samples were test pieces cemented with only CPC-Chem (Case CPC-Cont). Hereafter, the method of improving ground strength by adding CC powder to CPC-Chem is referred to as the CPC-CC method and SS powder to CPC-Chem is referred to as the CPC-SS method. The UCS of the test pieces removed from the mold container after curing was measured at an axial strain rate of 1%/min with the UCS apparatus T266-31100 (Seikensha Co., Ltd., Japan). In all cases two test pieces were tested.
The pH of the test pieces was calculated as an average of three measurements (top, bottom, and middle of each test pieces) using pH Spear (Eutech Instruments Pte., Ltd., Singapore). Segments of the UCS test pieces were observed by an SEM. The segments were naturally dried at 20°C for a few days and carbon-coated with a carbon coater. SEM observations were carried out at an accelerating voltage of 15 kV and at ×2000 magnification.

3. Results and Discussion

3.1 UCS of sand test pieces

In this study, Toyoura sand test pieces cemented by seven reaction mixture sets were chosen (adding CA : DPP = 0.6 M : 1.2 M mixture with no adding powders and adding CC and SS powders; the percentage of powders vary to 1, 5 and 10%). The measured UCS in this study ranged from 49.9 to 176.3 kPa. The maximum value was measured when the DPP/CA ratio was 1.2 M : 0.6 M with adding CC reagent 10% (Fig. 3(b)). The UCS tended to increase with the curing time for 14 days but after that the UCS value is decreased with the curing time for the samples with adding CC powder. In Fig. 3(a), the test pieces with SS-10% showed the value of UCS neither increasing nor decreasing after 14 days. In both figures, it says that the UCS tended to increase with the curing time for control samples (CPC-Cont). The test pieces with SS-10% showed that the UCS tended to decrease at 14 days curing period, it is assumed that some error could occur when preparing sample. To clarify this result, further examination of the test pieces is needed in the future. Also, the UCS value of the test pieces with SS-1% is higher than the UCS value of the test pieces with SS-5% but the UCS value of the test pieces with SS-10% is higher than SS-1 and 5% (Fig. 3(a)). Regarding the value of UCS, the difference between SS-1 and SS-5% is small. This is because the pH value is higher in SS-10% and then pH is high in SS-1% and pH is low in SS-5% (Fig. 4(a)). To clarify the reason for the decrease in pH in SS-5% test pieces, further examination of the test pieces in the CPC-SS method is needed in the future.

3.2 pH of sand test piece

For the CPC-Cont samples, the pH of the test pieces ranged from acidic to weakly alkaline (6.5–7.6), while the addition of SS-powder and CC-powder resulted in a strong alkaline (7.6–9.0) pH (Figs. 4(a) and 4(b)). The pH tended to increase with the time. Moreover, the pH value of CPC-SS samples is higher than pH values of CPC-CC samples (Fig. 5). Not only that, Fig. 5 comprises that the concentration of SS and CC powder increased, pH value is intended to increase. The results showed in Fig. 6(a) comprises when
curing time is increased, UCS is tended to increase and although, that the UCS tended to increase as the pH increase. Apparently the reason for this phenomena is the solubility of CPC become low when increase the pH (Fig. 1(b)) and the solubility of CPC is low means the CaCO3 precipitation is high.

When we considering CPC-Cont and CC-1% samples, it is utilized the following (Fig. 6(b)):

\[
\text{pH (CPC-Cont, 1 Day)}<\text{pH (CC-1%, 1 Day)}, \text{UCS (CPC-Cont, 1 Day)} = \text{UCS (CC-1%, 1 Day)}
\]

\[
\text{pH (CPC-Cont, 56 Day)} = \text{pH (CC-1%, 1 Day)}, \text{UCS (CPC-Cont, 1 Day)} > \text{UCS (CC-1%, 56 Day)}
\]

\[
\text{pH (CPC-Cont, 56 Day)}<\text{pH (CC-1%, 56 Day)}, \text{UCS (CPC-Cont, 56 Day)} > \text{UCS (CC-1%, 56 Day)}
\]

Considering that the solubility of CPC is dependent on its pH (Fig. 1) and results we taken it is summarized that the solubility is minimum at pH is about 8.

### 3.3 Effect of wet density on UCS

The measured wet density of the test pieces is provided in Figs. 7(a) and 7(b). The results shows, UCS value is increased with increase of density. Moreover, when curing time is increased the UCS is tended to increase. In addition, the increase of SS and CC powders %, wet density is increased. Since the density of CC powder (2.93 g/cm³) was greater than that of Toyoura sand (1.65 g/cm³), the density of the test pieces would increase with the mass% of CC powder and SS powder in the test pieces; we expected that the increase in density would result in an improvement in UCS. In the case of the test pieces treated by the CPC-CC and CPC-SS method, the increase in CC content increased the filling of voids between sand particles because of the increase in wet density.
3.4 SEM observation of sand test pieces

Figure 8 shows SEM images of seven sets of test samples. The crystal structures were not clearly observed in CPC-Cont, CPC-SS and CPC-CC samples. The samples which the precipitated CPC that enveloped the CC particles bonded with the surface of the sand particles; such bonding was also observed in sand test pieces, but without the formation of any crystal structure. The increase in UCS seemed to be because of the binding of the sand particles by the precipitated CPC that enveloped the CC particles. The analysis revealed that the improvement in UCS afforded by the CPC-CC and CPC-SS methods were because of the filling to the voids between sand particles and the uniting of the particles of cement material comprising Ca and P are stronger than CPC-Cont samples.

3.5 Effect on addition of SS and CC on the UCS of test pieces

Figure 3 shows the UCS test results. The UCS of test pieces cemented with CPC-SS and CPC-CC was larger than that for CPC-Chem alone, and it increased with time (Fig. 3). For the SS-10 samples in particular, the UCS was around 150 kPa after 1 day; it was nearly constant with the time except UCS after 14 days. It is assumed that some error could occur when preparing sample. To clarify this result, further examination of the test pieces is needed in the future.

The UCS of the CC-10 sample also increased from about 80 to 180 kPa and it remained at that level. Although the UCS of the CC-01 and CC-05 samples showed an increasing trend over 14 days, the UCS thereafter decreased. To clarify the reason for the decrease, further examination is needed in the future.

Practically the test pieces to which the SS and CC powder with 10% was added showed a UCS larger than 100 kPa. This statement recommends that through control of the CC content, the CPC-SS and CPC-CC method would allow for adjustment of strength according to the required strength properties of the ground while maintaining a UCS of over 100 kPa. In addition the improvement in UCS afforded by the CPC-CC and CPC-SS methods were because of the filling to the voids between sand particles and the uniting of the particles of cement material comprising Ca and P are stronger than CPC-Cont samples.

Considering results of UCS, pH, wet density and SEM images as discussed earlier, the governing factors for increase the strength of the sample are pH and wet density.

3.6 Merits of adding CC and SS powders

When considering up to 28 days curing period in Fig. 3, it is seemed that the UCS value for CPC-CC and CPC-SS method is higher than CPC-Cont. This is happened because of enhancement of strength of the samples by the addition of CC or SS powders. Therefore, it is one of merit for ground improvement by addition of CC and SS powders. However, after 56 days curing period the UCS value of adding powders is lower than no adding powders. Hence, the addition of powders not an advantage after 56 days. To clarify the reason for the decrease, further examination is needed in the future.

Finally, we consider about cost effectiveness of preparing samples. CPC solutions are very expensive. This paper aim is getting the strength more than 100 kPa. When the samples prepare with only adding CPC-Chem, it is need to increase the concentration of calcium and phosphate solutions. From this research using 0.6 M CA : 1.2 M DPP is not reached appropriate strength. If we increased the concentration of the solutions, the cost is also increased. However, we can get the same strength by using smaller amount (0.6 M CA : 1.2 M DPP) of CPC by adding CC or SS powders and the cost will be reduced. Hence, CPC-CC and CPC-SS method is cost effective technique than adding CPC-Chem only.
3.7 Differences between CC and SS powders

When comparing the differences between CC and SS powders, here consider UCS, pH and wet density parameters. In Fig. 3, the UCS value of SS-10% sample is nearly constant with the time. However, the UCS value of CC-10% sample is increased until 14 days curing period and then decreased with the time. Moreover, the UCS values of SS-1 and SS-5% are greater than the UCS values of CC-1 and CC-5% samples.

Regarding pH measurements, the results are not much differ between CPC-SS and CPC-CC method (Figs. 4(a) and 4(b)). Initially, the pH value of CPC-SS method is slightly high when comparing CPC-CC method. However, later the pH value is reached to nearly same value (nearly 9).

Next, the wet density is increased; CPC-Cont < SS and CC-1% < SS and CC-5% < SS and CC-10% (Figs. 7(a) and 7(b)). Although when density is increased, UCS value is intended to increase. However, the wet density of CPC-SS samples is less than CPC-CC samples.

Comparing above results, the CPC-SS method is more effective than CPC-CC method. However, it is difficult to get accurate conclusions using CPC-Chem solutions, because the structure of the solution is varied with time (Fig. 2).

3.8 Effect on addition of various CPC solutions (CA with DPP and DAP) on the UCS of test pieces

In this study, two reaction mixtures were selected; CA : DPP and CA : DAP with Ca/P ratio is 0.5. The test pieces were prepared adding CPC-Chem only, adding CPC-Chem with 5% CC and adding CPC-Chem with 5% SS. For this study, we reported from now powder percentage is 5%.

The measured UCS in this study is higher in the test pieces cemented by the addition of DAP than the addition of DPP for CPC-Cont, CPC-SS and CPC-CC method (Fig. 9). However, after 56 days curing period, the UCS of CPC-Cont sample cemented with DAP is decreased with the sample cemented with DAP (Fig. 9(a)). It is assumed that some error could occur when preparing sample. To clarify this result, further examination of the test pieces is needed in the future.

However, the pH values of the samples are reverses as UCS results, pH value of test pieces cemented with DAP is less than pH value of test pieces cemented with DPP (Fig. 10). Also, the pH value of test pieces cemented by both type of CPC-Chem solutions addition of CC and SS powders for is expected to increase with the increase of time (Fig. 11).

SEM images of test pieces subjected to DAP and DPP treatment with no adding powders are not clearly identify any
crystal structures (Fig. 12(a)). SEM images of test pieces subjected to DAP treatment with CC powders showed cuboid crystal formation and SS powders showed whisker-like crystal formation among particles of Toyoura sand (Figs. 12(b) and 12(c)). It has been reported that HA whiskers are formed by adding an acetic acid solution to amorphous calcium phosphate.20) In Portland cement, the formation of ettringite, which shows whisker-like crystals, promotes solidification and increases strength 21,22) These results suggest that the strength of the test pieces subjected to DAP treatment in this study might increase if whisker-like HA crystals are formed within them.

Considering results of UCS, pH and SEM images as discussed earlier, the governing factor for increase the strength of the sample is crystal formation. The most suitable combination of CA and phosphate stock solution concentrations for improving the strength of the UCS test piece was a DAP/CA ratio of 1.5 M : 0.75 M, for which the UCS reached a maximum of 137 kPa. Moreover, this research shown, it is difficult to get accurate results using CPC-Chem solutions, because the structure of the solution is varied with time (Fig. 2).

In this study, we begin by focusing on the development of novel grout material intended for sand and assume that the phosphate solution and calcium solution are mixed just before injection or that they are mixed in the ground after being sequentially injected. It is also necessary to conduct a detailed evaluation of the relationship between the UCS and the rate of stiffening because temporal variation in the UCS over the long term may prove to be one of the most important parameters in determining the applicability of CPC.

3.9 Applicability of CPC-powder method
In this study, we showed that CPC-powder has significant potential as a geotechnical material. The UCS of a sand test piece cemented with the CPC-powder method increased to a maximum of 156.9 kPa. The aim of the present study was to use CPC-Chem to achieve a maximum UCS of over 100 kPa, which is the strength required to prevent ground liquefaction. Using the CPC-powder method, we far exceeded this objective by achieving a UCS of over 150 kPa. When we considering many advantages and mechanical properties of CPC-powder method it is a good method for ground improvement technique.

Here we discuss about the applicability of CPC-powder method. The CPC-powder method can be applied to underpin existing foundations, create excavation support walls, create water cutoff walls and stabilize soils for tunneling. For underpinning applications, it is offers the advantages of being easily performed where access and space is limited, and of not requiring a structural connection to the foundation being underpinned.

Moreover this method we can use for deep soil mixing and for jet grouting which is an erosion replacement technology that can be used very effectively to create various geometries of stabilized soil, in-situ, for a wide range of applications. Other than that, for aggregate piers we can use this CPC-powder method. Aggregate piers are columns of compacted stone placed in situ which can be designed to reduce settlement, improve bearing capacity, mitigate liquefaction potential and increase shear resistance.

Also this mixture can use as an injection for expansive soils which is a method used for pre-swelling and/or stabilizing expansive clay soils. The addition of these
reagents can be extremely beneficial to improve bearing capacity, increase shear strength and expedite the workability of muddy construction sites and also it is use for soil fertilization.

4. Conclusion

In this study, our aim was to improve strength by adding CPC with scallop shell powder. This study aim was to exceed a maximum UCS of 100 kPa after 28 days of curing, but our expectation is achieved after 14 days of curing period. The results definite that the addition of powder increases the UCS of the test pieces. The UCS of test pieces cemented with CPC-Chem and calcium compound (SS and CC) powders significantly increased compared to cases where no powder was added to CPC-Chem. In particular, SS-01, SS-05, and SS-10 maintained a stable UCS of around 150 kPa for 56 days.

Fig. 11 Relationship between UCS and pH for test pieces with CPC-Cont, CC-5% and SS-5% for different curing days.

Fig. 12 (a) SEM images for test samples not adding powders, after 14 days (1-400× and 2-2000×). (A) CA : DAP = 0.75 M : 1.5 M (B) CA : DPP = 0.6 M : 1.2 M. (b) SEM images for test samples adding 5% of CC powders, after 14 days (1-400× and 2-2000×). (A) CA : DAP = 0.75 M : 1.5 M (B) CA : DPP = 0.6 M : 1.2. (c) SEM images for test samples adding 5% of SS powders, after 14 days (1-400× and 2-2000×). (A) CA : DAP = 0.75 M : 1.5 M (B) CA : DPP = 0.6 M : 1.2.

The CPC-powder method has the potential to be a non-contaminating and recyclable method for ground reinforcement that can satisfy the strength requirements for actual
ground while avoiding the problems of existing cement-based hardeners, and it may provide very interesting and unique properties for geotechnical and geo-environmental engineering. In addition, from this study it comprises, the governing factor for rising strength of samples can be pH or wet density or crystal formation or combination of these factors.

REFERENCES