Invited Paper

SOIL REINFORCEMENT USING CALCIUM PHOSPHATE COMPOUNDS

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Abstract

For the purpose of using calcium phosphate compounds (CPCs) for ground improvement measures, such as the reinforcement of soils and rocks, a fundamental examination of new grouting materials composed of CPCs (CPC-Chem) is required. Therefore, in this study, we have first analyzed the ideal conditions for CPC precipitation by *in vitro* examination of the different mixtures of calcium and phosphate stock solutions. Following that, Toyoura sand was cemented with CPCs and the cured specimens were analyzed by using unconfined compressive strength (UCS) tests. Similarly, Toyoura sand was cemented with a mixture of CPC-Chem and tricalcium phosphate (TCP) powder and then cured; these specimens too were then analyzed by using UCS tests. Test results indicate an improvement in UCS of TCP-added specimens when compared to that of no-additive (CPC-Chem alone) specimens. Besides, the morphology and elemental composition of the specimens were analyzed by using scanning electron microscopy (SEM) and energy dispersive X-ray fluorescence spectroscopy (EDX). The results obtained from the systematic analyses indicate the practical feasibility of using both the combination of CPC-Chem and TCP powder as well as the CPC-Chem alone as chemical grouts for ground improvement measures.

Keywords: Calcium phosphate compound, pH dependence, Seed crystal, Soil reinforcement, Unconfined compressive strength

Introduction

Engineers as well as scientists often learn and get inspired from nature. In nature, several types of minerals, such as calcium carbonate, calcium sulfate, calcium phosphate, calcium oxalate, silica, and iron oxide are innately precipitated by living things. These naturally occurring minerals, also known as “biominerals,” are considered promising materials for use in geological engineering, geotechnical engineering, and environmental geotechnics, because of their considerable strength and low environmental impact.

In this study, we have focused on the functionalities of calcium phosphate as a potential biomineral for use in ground improvement measures, such as the reinforcement of soils and rocks. In order to assess the feasibility, we have performed fundamental studies on the development of new grout materials composed of CPCs (CPC-Chem). CPCs exist as phosphate rocks (e.g., fluorapatite) in the natural environment, and as an important inorganic substance (i.e., hydroxyapatite, HA) in living things. CPCs possess unique physicochemical properties and offer several advantages, such as considerable mechanical strength, self-setting property [1], pH dependence of precipitation [1], non-toxicity, and recyclability, making them ideal for use as grout materials. In this study, we have first analyzed the ideal condition for CPC precipitation by *in vitro* examination of different mixtures of calcium and phosphate stock solutions. Subsequently, sand specimens were cemented with CPCs and the cured specimens were analyzed by using unconfined compressive strength (UCS) tests. Furthermore, sand specimens were cemented with a mixture of CPC-Chem and tricalcium phosphate (TCP) powder and the cured specimens were analyzed by using UCS tests. Test results indicate an improvement of UCS in TCP-added specimens when compared to that of non-additive (CPC-Chem alone) specimens. In addition, the morphology and elemental composition of the specimens were analyzed by using scanning electron microscopy (SEM) and energy dispersive X-ray fluorescence spectroscopy (EDX). Through these systematic analyses, this study aims to assess the practical feasibility of using CPC-Chem and a combination of CPC-Chem and TCP powders, as chemical grouts for improvement measures. A part of this paper has been published elsewhere [2, 3].

Materials and Methods

In Vitro CPC Precipitation Test

In this study, reagents with relatively high solubility were specifically chosen for convenient handling during practical application. Monoammonium phosphate (MAP) and diammonium phosphate (DAP) were used as the precursors for preparing phosphate stock solution. Similarly, calcium stock solution was prepared by using calcium nitrate (CN) or calcium acetate (CA).

The reaction mixtures were prepared by mixing 1:1 volume ratio (2 mL each) of ammonium phosphate (AP) solution and one of the two calcium stock solutions. The initial concentrations of the AP and CN solutions were 0.2, 1.0, 2.0, and 3.0 M, with the final concentrations of the reaction mixtures being 0.1, 0.5, 1.0, and 1.5 M. However, 3.0 M solution of MAP could not be prepared due to the limitations associated with the solubility of MAP. For the same reason, 2 M solution of CA could not be prepared for analysis. Accordingly, the concentrations of the CA stock solution were set as 0.2, 1.0, and 1.5 M, with the final concentrations of the reaction mixtures being 0.1, 0.5, and 0.75 M.

Subsequently, *in vitro* precipitation tests were conducted for the entire set of combinations of AP stock solutions and CN or CA stock solutions. The reaction mixtures were held at 20°C for 3 months, in order to monitor their precipitation status. During this time, we also measured the proportion of CPC precipitation volume to the reaction mixture volume (PPV). The maximum PPV was estimated to be 1.0. Simultaneously, we also measured the pH of the reaction mixture.

UCS Test of Sand Test Specimens Cemented with CPC-Chem

The reaction mixtures (sets of each stock solution) for the UCS test were selected according to the following three criteria, based on the results of the *in vitro* CPC precipitation test.

- Criterion 1: Set of stock solutions with the least concentration among the reaction mixtures with a PPV of 1.0.
- Criterion 2: Set of stock solutions with the maximum PPV among those with the maximum concentration.
- Criterion 3: Set of stock solutions with a concentration that is closest to the average of the concentrations discussed in criteria 1 and 2.

In this study, Toyoura sand with a particle density ρ_s of 2.64 g/cm^3 and mean particle diameter D_{50} of 170 μm was chosen for experimentation. The volume of the cylindrical test specimens made by using the mold container (φ = 5 cm, h = 10 cm) was 194.59 cm^3, and the maximum volume of the reaction mixture injected into the voids between the Toyoura sand particles was 73.3 mL. Based on these values, the reaction mixture was prepared by mixing 36.7 mL each of the DAP and calcium stock solutions.

The reaction mixture was uniformly mixed with a pre-determined quantity of Toyoura sand. This mixture was filled in the mold, and the sand in the mold was tamped down by using a hand rammer. Following that, the test specimens were cured at a temperature of 20°C under high humidity conditions for 1, 7, 14, and 84 days. The UCS of the test specimens after curing was measured at an axial strain rate of 1%/min. For each curing time, two test specimens were analyzed by performing the UCS test.

SEM Observation of Sand Test Specimens Cemented with CPC-Chem

Segments of UCS test specimens cemented with the reaction mixture with the maximum PPV value among the sets of AP and calcium stock solutions with the maximum concentration were observed by SEM. Simultaneously, elemental analyses of the segments were also performed by using energy dispersive X-ray fluorescence spectrometer (EDX) attached to the SEM.

UCS Test of Sand Test Specimens Cemented with CPC-Chem and TCP Powder

Regarding the choice of CPC powder, TCP powders with a particle density ρ of 3.14 g/cm^3 and mean diameter D_{50} of 12.0 μm were chosen as seed crystals from the various CPCs. Typically, TCP is insoluble in the neutral to weakly alkaline range of pH [1]. In addition, TCP is invulnerable to long-term contact with water, as it tends to transform into HA over time by the process of self-setting [1]. Furthermore, TCP is an approved food additive in Japan, implying that it is non-toxic and is readily available.

In this study, CPC-Chem was prepared by mixing DAP and CA in the concentration ratio of DAP:CA = 1.5 M:0.75 M. This yielded the best UCS among all the mixtures. Subsequently, the test specimens were prepared according to the combination ratios shown in Figure 1. In the typical process, 1% (3.2 g, TCP-01), 5% (16.0 g, TCP-05), and 10% (32.0 g, TCP-10) of TCP were added to 316.89 g, 304.09 g, and 288.09 g of Toyoura sand, respectively, so as to yield the weight of 320.09 g of a standard sand test specimen. Subsequently, CPC-Chem was added to the Toyoura sand and TCP mixture. It was uniformly mixed and filled in a mold container, similar to that performed for sand test specimens cemented with CPC-Chem. The test specimens were then cured at a temperature of 20°C under high humidity conditions for 28 days. In this study, three types of control samples were prepared for the analysis, namely, with deionized water only (DW-Cont), with CPC-Chem only (CPC-Cont), and with deionized water and TCP (TCP-Cont).

The UCS of the test specimens obtained by curing was measured at an axial strain rate of 1%/min. For DW-Cont and TCP-Cont, one test specimen was measured by the UCS test. For the other cases, two test specimens were examined. The pH of the test specimens was calculated as an average of three measurements (top, middle, and bottom of each test specimen).

Results and Discussion

In Vitro CPC Precipitation Test

CPC precipitation was observed in all the reaction mixtures analyzed in this study, as shown in Figure 2. In case of CN, the pH of the reaction mixture was in the range of 1.6–7.5, while that of CA was in the range of 4.6–7.9. The pH showed the highest values among all the combinations of AP and CN or CA, when DAP was used as AP.

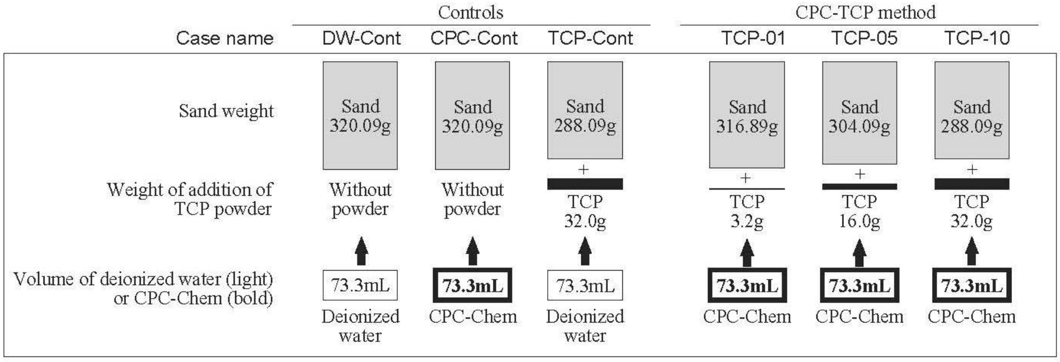

Figure 1. Conceptual image of making Toyoura sand test specimens

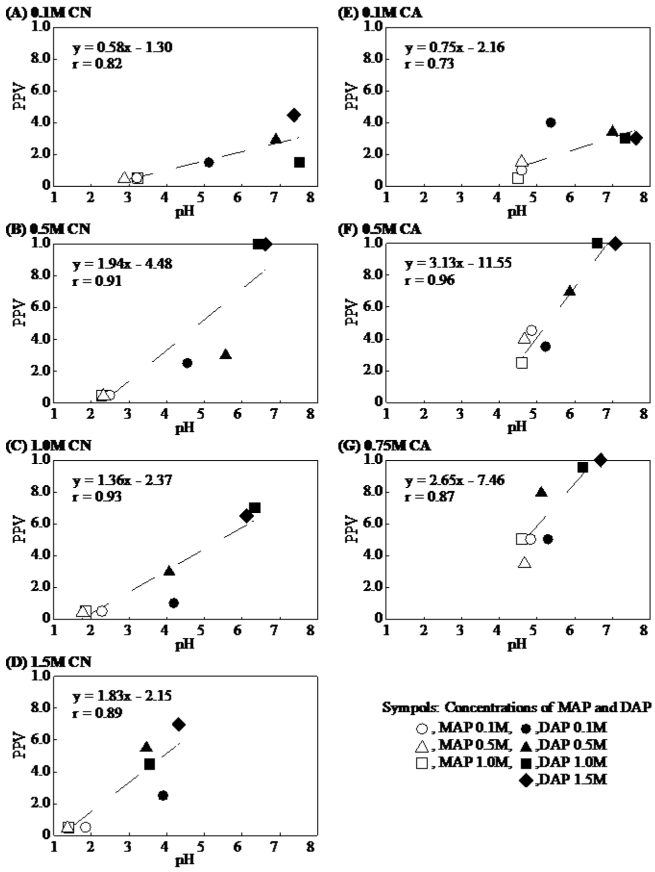

Figure 2. Relationship between the proportion of CPC precipitation volume of reaction mixture (PPV) and pH for calcium nitrate (CN) and calcium acetate (CA)

The results of the *in vitro* CPC precipitation test show that the PPV tends to increase with increase in pH from strongly acidic condition to neutral. This apparently explains the reason for the observed decrease in the solubility of the CPC at around neutral and weakly alkaline region [1]. The Ca/P molar ratios in all the reaction mixtures of each set were constant, regardless of the pH value. This indicates that the pH-increasing actions, including microbial activity such as urea hydrolysis of *Sporosarcina pasteurii* [4], can effectively promote the crystallization of CPC, upon injection of an acidic reaction mixture with little precipitation into soil and rock.

UCS Test of Sand Test Specimens Cemented with CPC-Chem

For UCS test, sand test specimens cemented by six different reaction mixture sets were selected for analysis, based on the results of the *in vitro* precipitation test (Figure 3). The measured UCS ranged from 10.2 to 87.6 kPa. The maximum UCS value was obtained in case of DPA/CA ratio of 1.5 M:0.75 M (Figure 3 (F)). As can be seen from the figure, UCS tends to increase with the curing time. However, test specimens with a DAP/CA ratio of 1 M:0.5 M showed a UCS of over 20 kPa, without any tendency to increase with curing time (Figures 3 (A) and (D)). The UCS values of the other reaction mixtures were below 20 kPa, and showed neither increasing nor decreasing trends as a function of the curing time.

Furthermore, the SEM images of test specimens subjected to CA treatment showed the formation of whisker-like crystals among the particles of Toyoura sand (Figure 4 (F)). It has previously been reported that HA whiskers are often formed when acetic acid solution is added to amorphous calcium phosphate [5]. In case of Portland cement, the formation of whisker-like crystals of ettringite promoted solidification and increases the overall strength of the cement [6]. Analogously, the formation of whisker-like HA crystals might increase the strength of the test specimens subjected to CA treatment. In addition, these results also suggest that CA is a potential candidate for preparing calcium stock solution for use in CPC-Chem.

On the other hand, the SEM image of the test specimens treated with CN (Figure 4 (C)) indicated the formation of plate-like crystals. Zhang et al. [7] have reported that the formation of plate-like HA is the characteristic of calcium stock solution formed by using CN. Besides, the precipitation of CPCs such as octacalcium phosphate (OCP) [8] and dicalcium phosphate (DCP) [5] can also lead to the formation of plate-like crystals. Moreover, non-HA CPC ultimately changes into HA over time [1]. Therefore, it can be assumed that the crystal form in test specimens treated with CN might ultimately change with prolonged curing period, thereby increasing the strength of the test specimens.

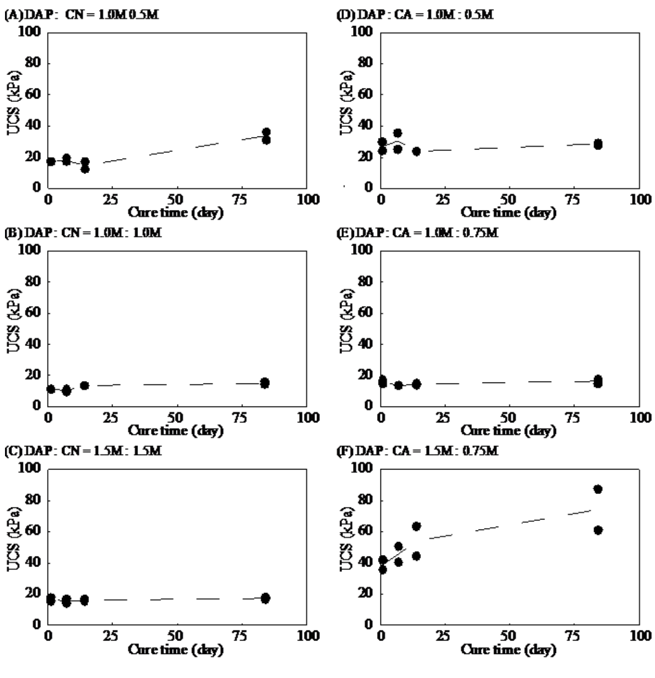

Figure 3. Temporal variations in unconfined compressive strength (UCS) of Toyoura sand test specimens cemented by CPCs

CPC-Chem is considered to have great potentials for use in geotechnical application [2]. Stock solutions can be prepared from fertilizers, and CPCs are a non-toxic, re-excavated mixture of soil, rock, and CPC grout. It is recyclable as an agricultural fertilizer or can be reused as CPC-Chem [2]. On the other hand, cement and cement-based hardening materials have the following limitations: large amount of carbon dioxide is released during the process of cement production, hexavalent chromium are often eluted from cement materials, excessive energy is needed for re-excavating the ground consolidated by cement, and the materials re-excavated from the cement-consolidated soil and rock are difficult to recycle. Given these considerations, it can be concluded that the use of CPC-Chem as a novel geotechnical material in ground improvement methods can avoid these recycling and contamination issues [2].

SEM Observation of Sand Test Specimens Cemented with CPC-Chem

Figures 4 (C) and (F) shows the SEM images of the segments of UCS test specimens, cemented by the reaction mixture with the maximum PPV among the sets of AP and calcium stock solutions with the maximum concentration. The SEM images captured at a magnification of ×76 indicate that the particles of Toyoura sand were covered with precipitation in both the CN and CA stock solutions (Figures 4 (A) and (D)). The SEM images captured at a magnification of ×600 indicate that the precipitates are formed as bridges between the particles of Toyoura sand (Figures 4 (B) and (E)). Increasing the magnification further to ×2000, plate-like crystals were observed in the segment cemented by CN stock solution (Figure 4 (C)). In contrast, a collection of whisker-like precipitates was formed in the segment cemented by the CA stock solution (Figure 4 (F)). Further elemental analysis of the precipitates indicates the overlapped distributions of phosphorous and calcium.

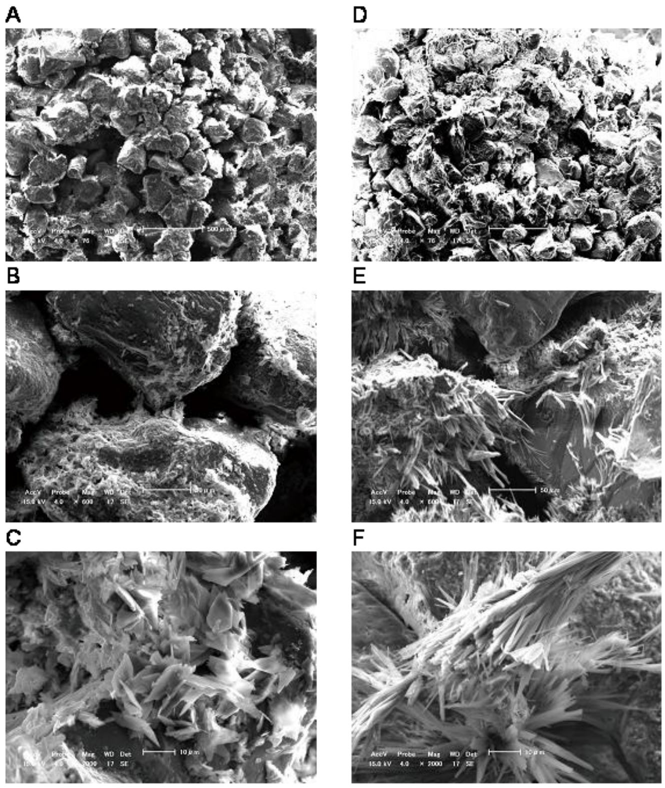

Figure 4. Scanning electron microscope (SEM) images of Toyoura sand test specimens cemented by diammonium phosphate and calcium nitrate (A, B, and C) or calcium acetate (D, E, and F)

UCS Test of Sand Test Specimens Cemented with CPC-Chem and TCP Powder

Figure 5 shows the results of the UCS test of sand test specimens cemented with CPC-Chem and TCP powder. In the figure, "N/A" indicates the non-availability of data. The UCS values of DW-Cont and TCP-Cont could not be obtained, as the two test specimens did not include cement materials and fractured owing to their self-weight. This confirmed the absence of pozzolanic properties in TCP, as the UCS of TCP-Cont was unobtainable. The TCP added test specimens of CPC-Chem (TCP-01, TCP-05, and TCP-10) exhibited higher UCS values than the controls (DW-Cont, CPC-Cont, and TCP-Cont). In case of TCP-05 and TCP-10, the UCS value exceeded 250 kPa, which is almost five times the UCS of CPC-Cont. Furthermore, the addition of TCP resulted in a maximum UCS of 100 kPa after 28 days of curing, which is the typical strength performance required as a countermeasure against ground liquefaction during earthquakes [9].

The pH of the test specimens with added TCP possessed was in the weakly acidic range (Figure 5). Using the pH dependence of the solubility of CPC [1], the mechanism of CPC biogrout (CPC-Bio) [10] can be used for increasing CPC precipitation. Here, the pH is increased by a pH-increasing reaction using microorganisms and ammonia sources, resulting in a further increase in the UCS. Further studies to analyze the effect of the TCP addition with a CPC-Bio cement on the UCS are underway.

The stress (σ)–strain (ε) curves of the specimen with the largest UCS from each test case are shown in Figure 6. The stress-strain curves of TCP-added test specimens had a distinctive peak at approximately 1% of the failure strain. Among the three TCP-added test specimens, TCP-05 had a UCS of over 250 kPa and relatively cost-effective than TCP-10. Accordingly, TCP-05 composition is considered to be effective, economical, and optimal. However, the results are merely based on the UCS data obtained after 28 days of curing. The long-term performance of the sand test specimens, including TCP-05 that is treated with CPC-Chem and TCP, should be proven in the future.

In this study, the UCS of a sand test specimen cemented with CPC-Chem and TCP powder (also referred to as the CPC-TCP method) reached 261.4 kPa. The CPC-TCP method can be further improved by considering other compositions, such as different phosphate and calcium stock solutions, and also by expending the activity of microorganisms. Considering the concentration of the phosphate stock solution (1.5 M), it is also thought that a gel-like or amorphous CPC will precipitate immediately upon mixing CPC-Chem and sand, which tends to temporally self-set as HA up over the curing time period of 28 days. To understand the expression mechanism of the UCS resulting from the CPC-TCP method and to use the method more effectively, the temporal relation between the crystal species and the UCS should be investigated in detail. Besides phosphate, other materials could also contribute to the effective use of industrial waste and byproducts. Therefore, the compatibility between CPC-Chem and other potential materials should also be examined.

Conclusions

The main conclusions drawn from this study are as follows:

- A potential cement type calcium phosphate compound, which is capable of increasing the UCS of the sand test specimen with time, was identified by evaluating the effect of pH, the type of phosphate and calcium stock solutions, and the component ratios of phosphate stock solution on the PPV of CPC.
- CPCs are suitable candidates for use as CPC-Chem owing to their self-setting property, and also as CPC-Bio because of their crystal structure and the pH dependence of precipitation.

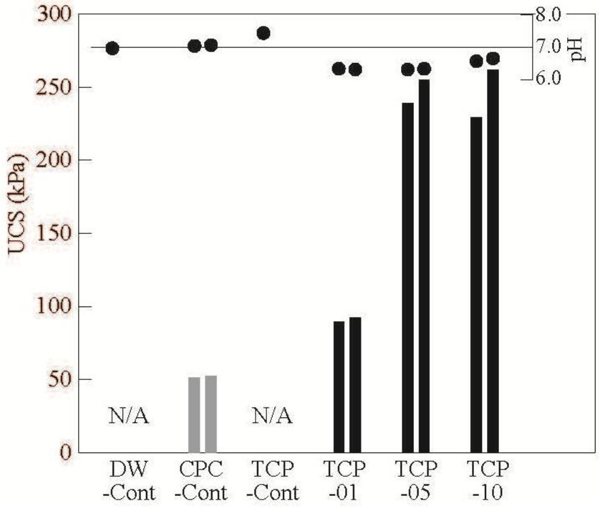

Figure 5. Unconfined compressive strength (UCS) and pH of Toyoura sand test specimens

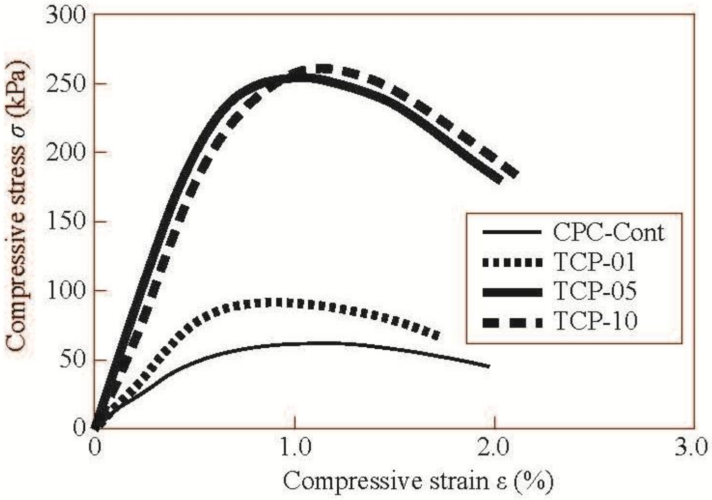

Figure 6. Stress (σ)–strain (ε) curves of Toyoura sand test specimens (only the highest unconfined compressive strength (UCS) was shown in each case)

- The UCS of the test specimens cemented using the CPC-TCP method reached over 100 kPa, which is the targeted value for use in geotechnical applications. The UCS value further increased to a maximum of 261.4 kPa, upon 28 days of curing. The increase in UCS value was significantly higher when compared to that of non-additive test specimens.

The pH of the test specimens cemented using the CPC-TCP method was weakly acidic. Considering the pH dependence on the solubility of CPC, the CPC-TCP method could potentially be extended to CPC-Bio by utilizing the pH-increasing activity of microorganisms.

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