Unique Grout Material Composed of Calcium Phosphate Compounds

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ABSTRACT: To employ calcium phosphate compounds (CPCs) in ground improvement measures such as the reinforcement of soil and rock, we examined suitable conditions for CPC precipitation and performed unconfined compressive strength (UCS) tests of sand test pieces cemented by CPC. Two types of phosphate stock solution and two types of calcium stock solution were used to prepare the reaction mixtures and CPC precipitation was confirmed in all reaction mixtures. The volume of CPC precipitation in the mixture increased as the pH rose from strongly acidic to around neutral. The UCS of sand test pieces cemented by 1.5 M diammonium phosphate and 0.75 M calcium acetate tended to increase with time, reaching a maximum of 87.6 kPa. The results indicate the practical feasibility of using unique and new CPC grouts as chemical grouts because of their self-setting property and as biogrouts because of the pH dependence of precipitation.

Keywords: Calcium Phosphate Compound, Grout Material, Unconfined Compressive Strength, Self-setting

1. INTRODUCTION

Novel grout materials have been developed to reinforce the ground and/or to control ground permeability with bacterially produced cement material [1]–[6]. These grout materials are called biogrouts. Three mechanisms of mineral formation have mainly been considered for biogrouts. The first mechanism is the precipitation of calcium carbonate by in situ microorganisms and/or added yeasts [2]. In this process, calcium carbonate is precipitated by the binding of carbonate ions released from microorganisms and calcium ions from the grout, which includes calcium and glucose. The second mechanism was reported by Whiffin et al. [3], who used urea instead of glucose and ureolytic *Sporosarcina pasteurii* instead of yeast and other in situ microorganisms; the decomposition of urea by *S. pasteurii* produced carbon dioxide, which supplied the carbonate ions. In both cases, additional pH buffers or ammonium ions play the role of pH adjusters for effective precipitation. The third mechanism is based on the pH dependence of the extension speed of the siloxane bond; this mechanism was reported by Terajima et al. [5], who utilized the carbon dioxide produced by yeast to neutralize the alkaline active silica solution because the siloxane bond rapidly extends and gelates in the middle range of pH.

Soil and rock vary infinitely in their physical and chemical properties. This fact orients the development of biogrout along two main directions: one, to develop a highly general-purpose biogrout, and the other, to develop a specialized biogrout for a specific type of soil or rock. To apply biogrout to various soils and rocks, it is very important to increase the number of mechanisms available for the precipitation of cement materials.

In engineering as well as in science, it is essential to learn from nature. In nature, various minerals, such as calcium carbonate, calcium sulfate, calcium phosphate, calcium oxalate, silicate, and iron oxide are precipitated by living organisms. These biominerals are promising as engineering materials because they have considerable strength and low environmental impact. In this study, we carried out a fundamental examination on novel grout materials composed of calcium phosphate compounds (CPCs) (Fig. 1). CPCs exist as phosphate rocks (e.g., fluorapatite) in the natural environment and also as an important inorganic substance (e.g., hydroxyapatite, HA) in living organisms [7]. As shown in Table 1, there are 11 known CPCs with various calcium-to-phosphate (Ca/P) molar ratios in the ternary system $Ca(OH)_2$–H_3PO_4–H_2O. Research and development of materials composed of CPCs are currently in progress, especially in the fields of medicine and dentistry.

Medical CPC paste, however, is extremely expensive and has high viscosity, which makes it unfeasible for engineering applications. Therefore, we considered CPC use from an engineering viewpoint and aimed to develop a grout material that could be precipitated under normal temperature and pressure through microbial activity by using materials that can be easily handled. To the best of our knowledge, no existing grout material makes use of the self-setting mechanism of CPC alone or employs microbial pH adjustment activity for CPC precipitation. CPCs have unique physical and chemical properties. Their numerous advantages as a grout material include the following:

(1) Gel-like or amorphous CPCs change into HA over time (Fig. 2 [8]). Therefore, CPC hardens after injection into soil and rock because of the self-setting mechanism.

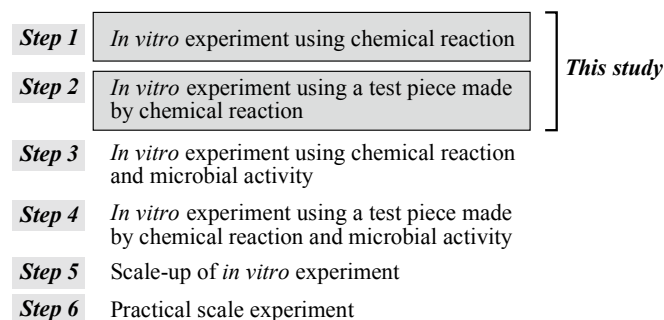|		
Step 1	*In vitro* experiment using chemical reaction	This study
Step 2	*In vitro* experiment using a test piece made by chemical reaction	
Step 3	*In vitro* experiment using chemical reaction and microbial activity	
Step 4	*In vitro* experiment using a test piece made by chemical reaction and microbial activity	
Step 5	Scale-up of *in vitro* experiment	
Step 6	Practical scale experiment	

Fig. 1 Flowchart of the study. The steps carried out in this study are highlighted in gray.

Table 1 Properties of biologically relevant calcium orthophosphates. The table is adapted from Dorozhkin and Epple [7].

Ca/P ratio	Compound	Abbreviation	Formula
0.5	Monocalcium phosphate monohydrate	MCPM (MCP)	$Ca(H_2PO_4)_2·H_2O$
0.5	Monocalcium phosphate anhydrate	MCPA (MCP)	$Ca(H_2PO_4)_2$
1.0	Dicalcium phosphate dihydrate	DCPD (DCP)	$CaHPO_4·2H_2O$
1.0	Dicalcium phosphate anhydrate	DCPA (DCP)	$CaHPO_4$
1.33	Octacalcium phosphate	OCP	$Ca_8(HPO_4)_2(PO_4)_4·5H_2O$
1.5	α-tricalcium phosphate	α-TCP	$α-Ca_3(PO_4)_2$
1.5	β-tricalcium phosphate	β-TCP	$β-Ca_3(PO_4)_2$
1.2-2.2	Amorphous calcium phosphate	ACP	$Ca_x(PO_4)_y·nH_2O$
1.5-1.67	Calcium-deficient hydroxyapatite	CDHA	$Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}$ $(OH)_{2-x}$ $(0 < x < 1)$
1.67	Hydroxyapatite	HA	$Ca_{10}(PO_4)_6(OH)_2$
2.0	Tetracalcium phosphate	TTCP	$Ca_4(PO_4)_2O$

(2) The solubility of CPCs depends on the pH of the surrounding environment (Figs. 3 [8] and 4). This makes it possible to utilize the mechanisms of pH adjustment by microorganisms, which are used in known biogrout methods to control CPC precipitation.

(3) Phosphate and calcium stock solutions can be made from fertilizers, and calcium and phosphate can also be extracted from the bones of livestock and the shells of aquatic animals, respectively.

(4) CPCs that precipitate after grout injection are non-toxic.

(5) Unlike concrete, re-excavated muck that consists of soil, rock, and CPC grout is recyclable as agricultural fertilizer.

We begin by focusing on the development of a novel grout material intended for soil materials (sand, in this study). We then extend our approach to control the strength and permeability of rock materials. This work can contribute to countermeasures for liquefaction in alluvial plains and reclaimed land, and to measures for preventing the failure of natural and/or artificial slopes.

In this study, the most suitable conditions for CPC precipitation were determined in an in vitro examination by using phosphate and calcium stock solutions (Step 1 in Fig. 1). Subsequently, test pieces composed of sand cemented by CPC were subjected to unconfined compressive strength (UCS) tests and observed by scanning electron microscopy (SEM) (Step 2 in Fig. 1). Our aim was to evaluate the feasibility of using the unique and novel grout as both a chemical and a microbiological grout by exploiting the self-setting property of CPC and the microbial pH adjustment activity in CPC precipitation, respectively.
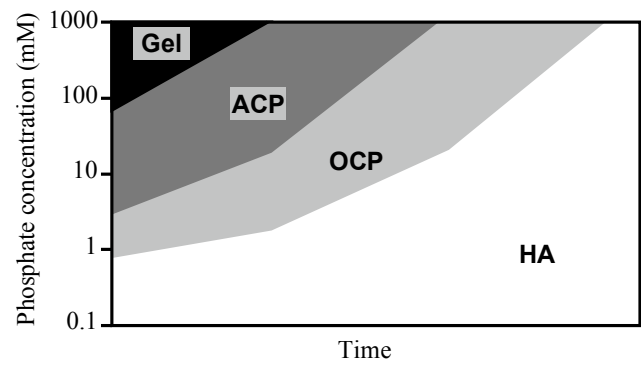

Fig. 2 Formation, stability, and hydrolysis of calcium phosphates as a function of phosphate concentration (log(P)) in solutions of amorphous calcium phosphate (ACP) at neutral pH. OCP, octacalcium phosphate; HA, hydroxyapatite. The figure is adapted from Tung [8].
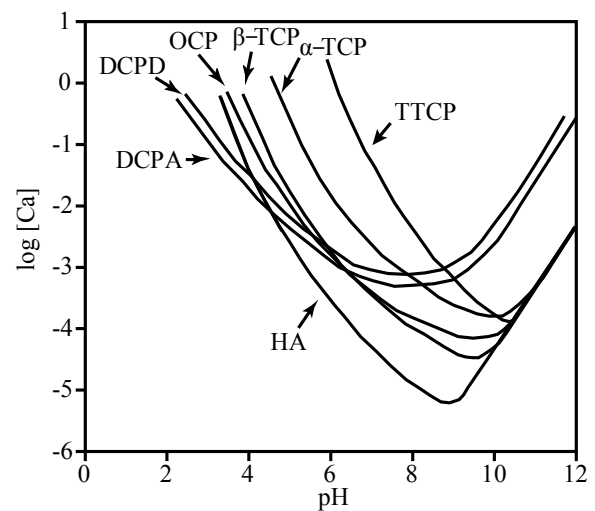

Fig. 3 Solubility phase diagrams for the ternary system, $Ca(OH)_2$–H_3PO_4–H_2O, at 25 °C, showing the solubility isotherms of $CaHPO_4$ (DCPA), $CaHPO_4·2H_2O$ (DCPD), $Ca_8H_2(PO_4)_6·5H_2O$ (OCP), $α-Ca_3(PO_4)_2$ (α-TCP), $β-Ca_3(PO_4)_2$ (β-TCP), $Ca_4(PO_4)_2O$ (TTCP), and $Ca_{10}(PO_4)_6·$ $(OH)_2$ (HA). The figure is adapted from Tung [8].
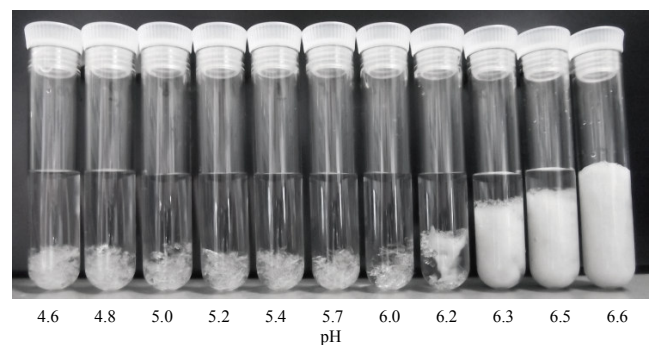

Fig. 4 Effect of pH on the precipitation volume of CPC.

2. MATERIALS AND METHODS

2.1 CPC Precipitation Test

Reagents with relatively high solubility were chosen for convenient handling in a practical application. Monoammonium phosphate (MAP, pH 4.2) and

diammonium phosphate (DAP, pH 8.0) were used as the components of the phosphate stock solution—a type of agricultural fertilizer that can be prepared easily. For the calcium stock solution, calcium nitrate (CN) or calcium acetate (CA) was used. All reagents were of special grade.

The reaction mixtures were prepared by mixing the ammonium phosphate (AP) solution and one of the two calcium solutions at a 1:1 volume ratio (2 mL each); consequently, the final concentrations of the AP and calcium stock solutions were half the initial concentrations. The initial concentrations of the AP and CN solutions were 0.2, 1.0, 2.0, and 3.0 M (the final concentrations were 0.1, 0.5, 1.0, and 1.5 M). A 3.0 M MAP solution could not be prepared because the water solubility of MAP at 20 °C is 27.2 g/100 g. The solubility of calcium acetate is 25.8 g/100 g water (20 °C). Because we could not prepare a 2 M solution of calcium acetate, the concentrations of the CA stock solution were set at 0.2, 1.0, and 1.5 M (the final concentrations were 0.1, 0.5, and 0.75 M). The in vitro precipitation tests were conducted for the entire set of combinations of AP stock solutions and CN or CA stock solutions.

Subsequently, the reaction mixtures were left standing at 20 °C for 3 months to monitor their precipitation status; a period of 3 months was chosen because changes in this status can appear with time depending on the properties of the CPC. To observe the precipitation status, the proportion of the CPC precipitation volume to the reaction mixture volume (PPV) was measured during this time (the maximum PPV was 1.0). Simultaneously, the pH of the reaction mixture was measured by using a pH Spear, a device designed for measuring the pH of solids and semisolids, including gels.

2.2 UCS Test of Sand Test Pieces Cemented by CPC

Reaction mixtures (sets of each stock solution) for the UCS test (Fig. 5) were selected according to three criteria, based on the results of the in vitro CPC precipitation test.

Criterion 1: Set of stock solutions with the minimum concentration among reaction mixtures that showed a PPV of 1.0 (DAP/CN = 1.0 M:0.5 M, DAP/CA = 1.0 M:0.5 M).

Criterion 2: Set of stock solutions with the maximum PPV among those with the maximum concentration (DAP/CN = 1.5 M:1.5 M, DAP/CA = 1.5 M:0.75 M).

Criterion 3: Set of stock solutions with a concentration that is closest to average of the concentrations discussed in criteria 1 and 2 (DAP/CN = 1.0 M:1.0 M, DAP/CA = 1.0 M:0.75 M).

Table 2 lists the physical properties of the Toyoura sand used as a soil material in this study. To avoid the destruction of the test pieces during their removal from the mold, the inner wall of the mold container (φ = 5 cm, h = 10 cm) was covered with a 0.01-cm-thick overhead projector (OHP) sheet. The volumes of the test pieces made by the mold container and maximum volume of the reaction mixture injected into the voids between the Toyoura sand particles were 194.59 cm^3 and 73.3 mL, respectively. Considering these values, 36.7 mL each of the DAP and calcium stock solutions were mixed, making their final
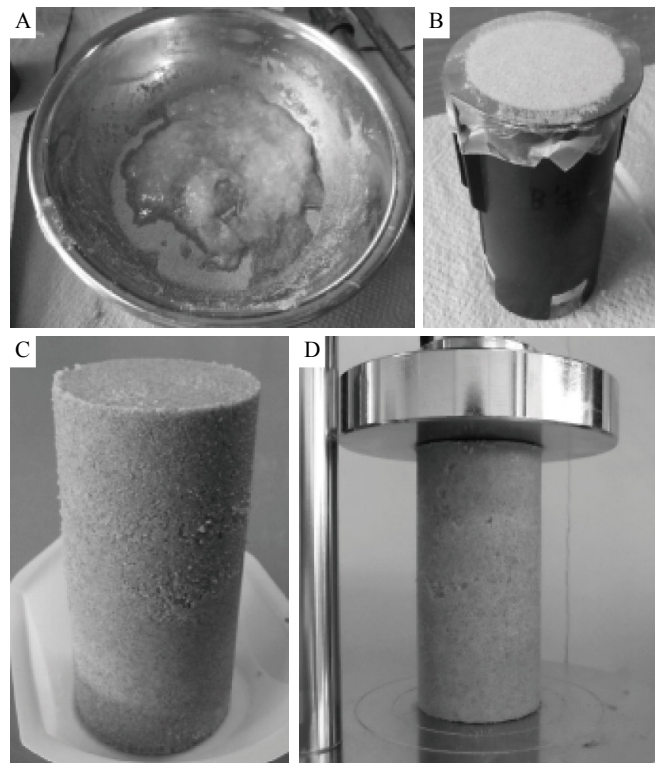

Fig. 5 Toyoura sand test pieces cemented by CPC. A, mixing stock solutions and Toyoura sand; B, a test piece covered with Parafilm; C, a self-standing test piece cemented by CPC; D, UCS test.

Table 2 Physical characteristics of Toyoura sand.

Soil particle density, ρ_s (g/cm^3)	2.64
Minimum density, ρ_{dmin} (g/cm^3)	1.335±0.005
Maximum density, ρ_{dmax} (g/cm^3)	1.645±0.010
Maximum void ratio, e_{max}	0.973
Minimum void ratio, e_{min}	0.609
Mean grain size, D_{50} (mm)	0.17
10% diameter on grain size diagram, D_{10} (mm)	0.11
Fine fraction content, Fc (%)	0

concentrations half of their initial concentrations. Immediately after the reaction mixture was prepared, it was uniformly mixed with weighted Toyoura sand in a stainless-steel ball for 2 min. This mixture was divided into quarters, each of which was placed into a mold with an OHP sheet. 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. Finally, the edge surface of the test piece was molded flat and covered with Parafilm M to avoid desiccation. The test pieces were cured in an airtight container at a high humidity for 1, 7, 14, and 84 days at 20 °C. The UCS of the test pieces removed from the mold container after curing was measured at an axial strain rate of 1 %/min by employing a UCS apparatus. For each curing time, two test pieces were used to perform the UCS test.

2.3 SEM Observation of Sand Test Pieces Cemented by CPC

Segments of UCS test pieces cemented by 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. The segment of the

test piece was allowed to dry naturally at 20 °C for a few days and was then carbon-coated by a carbon coater. SEM observations were carried out at an accelerating voltage of 15 kV and at ×2000 magnification. Simultaneously, elemental analyses of test piece segments were performed by using an energy dispersive X-ray fluorescence spectrometer (EDX) with SEM.

3 RESULTS

3.1 CPC Precipitation Test

CPC precipitation was observed in all reaction mixtures (Fig. 6). The pH of the reaction mixture ranged from 1.6 to 7.5 for CN and from 4.6 to 7.9 for CA. The pH showed the highest values among all combinations of AP and CN or CA when DAP was used as AP. The PPV showed a tendency to increase with the pH.

3.2 UCS Test of Sand Test Pieces Cemented by CPC

Toyoura sand test pieces cemented by six reaction mixture sets were selected based on the results of an in vitro precipitation test (Fig. 7). The measured UCS in this study ranged from 10.2 to 87.6 kPa. The maximum value was measured when the DPA/CA ratio was 1.5 M:0.75 M (Fig. 7 (F)). The UCS tended to increase with the curing time.

Test pieces 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. The UCS values of the other four reaction mixtures were below 20 kPa and showed neither increasing nor decreasing trends as a function of the curing time.

3.3 SEM Observation of Sand Test Pieces Cemented by CPC

Segments of UCS test pieces cemented by the reaction mixture with the maximum PPV among the sets of AP and calcium stock solutions with the maximum concentration were observed by SEM (Figs. 7 (C) and (F)). In images captured at ×76 magnification, particles of Toyoura sand were covered with precipitation in both the CN and CA stock solutions (Figs. 8 (A) and (D)). In images captured at ×600 magnification, bridges built between particles of Toyoura sand by precipitation were observed (Figs. 8 (B) and (E)). At ×2000 magnification, plate-like crystals with diameters of ~10 μm were observed in the segment cemented by CN stock solution (Fig. 8 (C)). In contrast, a collection of whisker-like precipitations was formed in the segment cemented by the CA stock solution (Fig. 8 (F)). Through elemental analysis, it was found that the distributions of phosphorous and calcium overlapped and corresponded to the distribution of precipitation in the SEM images.
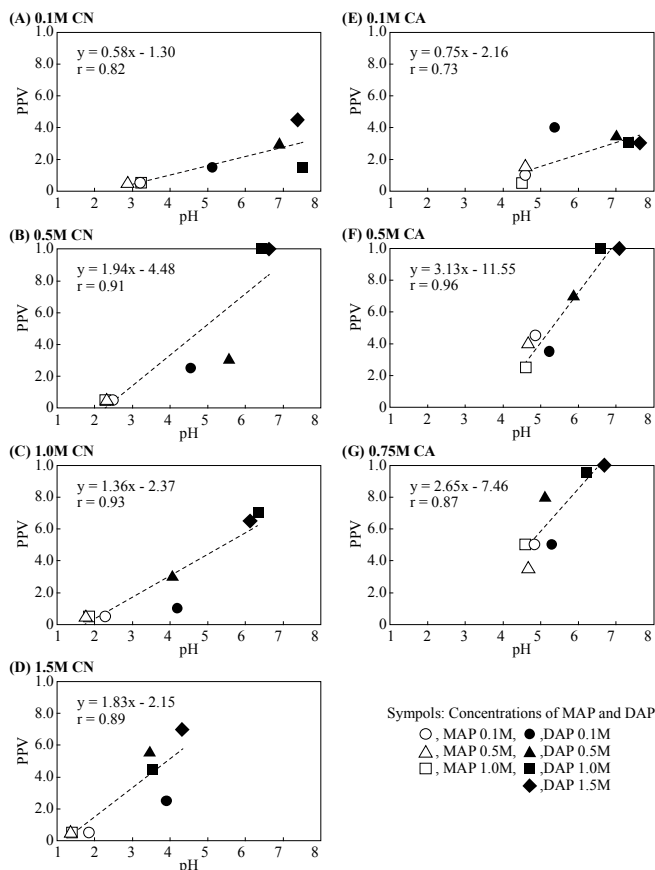

Fig. 6 Relationship between the proportion of CPC precipitation volume of reaction mixture (PPV) and pH for calcium nitrate (CN) and calcium acetate (CA). The value is represented as the proportion of the precipitation volume to the entire volume of the reaction mixture (4 mL). In vitro precipitation test was carried out by mixing equal volumes of ammonium phosphate and calcium nitrate or calcium acetate solutions.
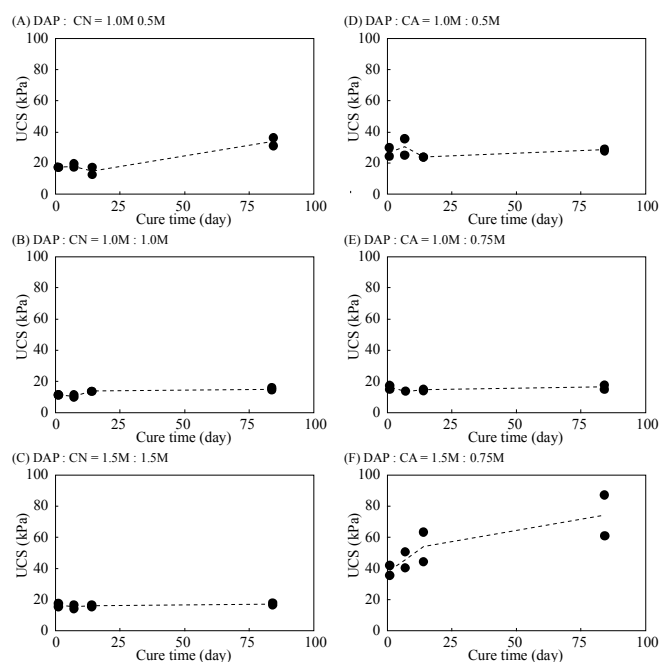

Fig. 7 Temporal variations in unconfined compressive strength (UCS) of Toyoura sand test pieces cemented by CPCs. Mixing concentrations of diammonium phosphate (DAP) and calcium solutions (calcium nitrate (CN) and calcium acetate (CA)) for mixture of each grout: (A), 1.0 M:0.5 M; (B), 1.0 M:1.0 M; (C), 1.5 M:1.5 M; (D), 1.0 M:0.5 M; (E), 1.0 M:0.75 M; (F), 1.5 M:0.75 M. The dashed line represents the change in the average of two measurements.
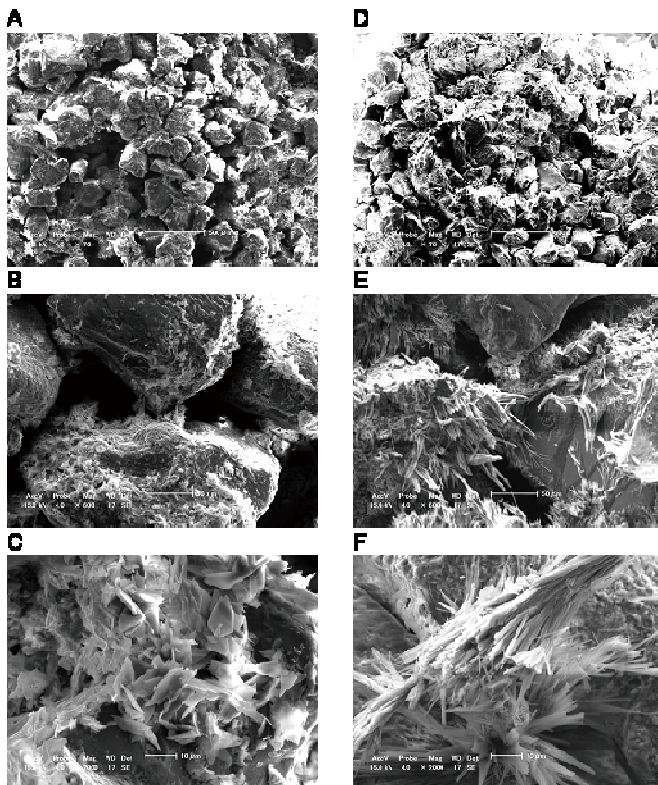
Fig. 8 Scanning electron microscope (SEM) images of Toyoura sand test pieces cemented by diammonium phosphate and calcium nitrate (A, B, and C) or calcium acetate (D, E, and F). A and D, ×76; B and D, ×600; and C and F, ×2000. An accelerating voltage of 15 kV was used for the observations. Bars represent 500, 50, and 10 μm in A and D, B and E, and C and F, respectively.

4 DISCUSSION

4.1 Relationship between CPC Precipitation and pH of Reaction Mixture

The results of an in vitro CPC precipitation test showed that the PPV tended to increase as the pH increased from strongly acidic to around neutral. Apparently, this is why the solubility of the CPC decreased at around neutrality and in a weakly alkaline region [8]. The Ca/P molar ratios in all reaction mixtures of each set were constant, regardless of pH. This indicates the possibility that pH-increasing actions, including microbial activity, e.g., urea hydrolysis of *S. pasteurii* [3], can effectively promote crystallization of CPC after the injection of an acidic reaction mixture with little precipitation into soil and rock.

In the case of 1.5 M CN (Fig. 6 (D)), the pH of the reaction mixture was below 4, even at the maximum PPV. This shows that if calcium is saturated, CPC can be precipitated in acidic conditions under which the solubility of CPC is higher. Some types of peat soils, which typically form a poor ground surface, show acidic properties due to the presence of humic acid [9]. The above results demonstrate the suitability of applying the CPC grout to such a soil. Because the solubility of CPC is also higher in alkaline regions around pH 12, a high concentration of calcium can be achieved in such alkaline conditions [10]. The mechanism proposed by Kawasaki et al. [2] of utilizing acidification by carbon dioxide from yeasts may precipitate a large amount of CPC if an alkaline stock solution is initially used. In this case, it is necessary to study the utilization and activation of alkali-tolerant yeasts and bacteria.

4.2 UCS Improved by CPC

The most suitable combination of AP and calcium stock solution concentrations for improving the strength of the UCS test piece was a DAP/CA ratio of 1.5 M:0.75 M (Fig. 7 (F)), for which the UCS reached a maximum of 87.6 kPa. In contrast, all UCS values of the test pieces subjected to CN treatment were below 20 kPa and showed no significant trends (Figs. 7 (A)–(C)). SEM images of test pieces subjected to CA treatment showed whisker-like crystal formation among particles of Toyoura sand (Fig. 8). It has been reported that HA whiskers are formed by adding an acetic acid solution to amorphous calcium phosphate [11]. In Portland cement, the formation of ettringite, which shows whisker-like crystals, promotes solidification and increases strength [12]. These results suggest that the strength of the test pieces subjected to CA treatment in this study might increase if whisker-like HA crystals are formed within them. In addition, they show that CA would be a potent candidate calcium stock solution in applications of CPC grout. In contrast, plate-like crystals were formed in test pieces treated with CN (Fig. 8). Zhang et al. [13] reported that plate-like HA formed in cases where CN was used as the calcium stock solution. There are a few CPCs, e.g., octacalcium phosphate (OCP) [14] and dicalcium phosphate (DCP) [11], whose precipitation leads to plate-like crystals. Non-HA CPC ultimately changes into HA [8]. Thus, the crystal form in test pieces treated with CN may change after a long curing period, thereby increasing the strength of the test pieces.

Whiffin et al. [3] reported that the precipitation of at least 60 kg/m^3 of calcium carbonate is required to achieve a measurable strength improvement in a sand test piece (porosity, 37.8%) by using biogrout. Assuming that HA (Ca/PO_4/OH molar ratio of 5:3:1) precipitates maximally in the most porous of the Toyoura sand test pieces, the theoretical value of CPC precipitation in 73.3 mL of the reaction mixture was 5.5 g in the test piece shown in Fig. 7 (F) (porosity, 37.7%). The details of this piece, which is cemented with a DAP/CA ratio of 1.5 M:0.75 M, are as follows:

(1) 0.75 M Ca corresponds to ~2.2 g of Ca mass
(2) 0.45 M PO_4 corresponds to ~3.1 g of PO_4 mass
(3) 0.15 M OH corresponds to ~0.2 g of OH mass

The volume of the Toyoura sand test piece was 194.59 cm^3; therefore, the proportionate CPC precipitation mass for a volume of 1 m^3 is 28.3 kg. This means that the CPC grout attained a UCS of 87.6 kPa by a relatively low amount of CPC precipitation. A surplus of phosphate may exist in the pore water of the test pieces treated with CA because HA has a calcium-phosphorus molar ratio of 1.67 (Table 1). This suggests that multiple injections of calcium stock solution increase HA precipitation and induce the strengthening of test pieces, as described previously [6].

In this study, we begin by focusing on the development of novel grout material intended for soil materials (sand, in this study) 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. The procedure for mixing them might be formulated based on the viscosity of the reaction mixture, the PPV of CPC

precipitation, and the precipitation status over time for a particular combination of stock solutions. 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.

4.3 Application of Knowledge in and Collaboration with Medical and Dental Sciences

The feasibility of improving the UCS was examined by forming CPC with only solutions that can be conveniently handled during practical application. Chow [15] reported that the utilization of CPC seed crystal caused the strengthening of HA in CPC solution. In particular, Chow [15] pointed out that utilization of a powder mixture of TTCP (tetracalcium phosphate) and DCP led to a stronger HA with the greatest purity. The pastes also possessed the properties of self-setting and biocompatibility.

Research on CPC paste has established that a maximum compressive strength of 56 MPa can be obtained with a mixture of DCP and α-TCP (α-tricalcium phosphate) pastes and a seed crystal of calcium carbonate; this is substantially larger than the compressive strength of 35 MPa obtained without the seed [16]. This observation shows that the presence of the calcium carbonate seed crystal can supplement the effect of strength reinforcement, as is the case for the CPC grout studied here. Co-existing ions (e.g., magnesium ions) with in situ pore water change the form of the CPC crystal [17], and the compressive strength of HA is increased by the co-existence of bone marrow cells and CPC [18]. These observations suggest that the effective utilization of ionic and/or organic materials can be an important method for strength reinforcement in the geotechnical field.

Nowadays, clinical breakthroughs are made daily in the medical and dental sciences; these include the enhancement of the injectable [19], biocompatibility, and self-setting properties of CPC paste by organic matter [20] as well as the development of novel apatite blocks [21]. The injectability of CPC grout is also one of the most important factors in its application to natural soils and rocks with minute cracks. The medical and dental sciences have accrued an extensive amount of fundamental knowledge regarding CPC.

5 CONCLUSION

In this study, we examined the feasibility of a new grout material composed of CPC. A candidate cement type that increased the UCS of the sand test piece with time was identified by evaluating the effect of pH, the type of phosphate and calcium stock solutions, and the component ratios of the phosphate stock solution on the PPV of CPC. Although only chemical reactions for CPC precipitation were examined, the results of this study showed that CPCs have sufficient potential for use as (1) chemical grouts, because of their self-setting property, and (2) biogrouts, because of their crystal structure and the pH dependence of precipitation.

Changes in the concentration of the reaction mixture were not reflected proportionally in the strength of the sand test pieces. In the future, additional tests aimed at determining the improvement in the strength by CPC are needed to understand more clearly the underlying mechanical processes and to facilitate practical application. The relationship between the strength and the various CPC precipitation parameters (concentration and pH of reaction mixture, curing time, etc.) should be examined in further detail, as continued research is needed to identify the process or processes that link crystal precipitation to the increase in strength. Furthermore, shearing and permeability tests using pieces cemented by CPC should be conducted to evaluate the applicability of CPCs for purposes such as permeability control and reinforcement of soil and rock.

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