Enhancement of unconfined compressive strength of sand test pieces cemented with calcium phosphate compound by addition of various powders

S. Kawasaki[a,*], M. Akiyama[b]

[a]*Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan*
[b]*Geoscience Research Laboratory Co., Ltd., 1794 Kamiwada, Yamato, Kanagawa 242-0014, Japan*

Abstract

To improve the unconfined compressive strength (UCS) of a novel chemical grout composed of a calcium phosphate compound (CPC-Chem), we performed UCS tests and scanning electron microscopy (SEM) observations on sand test pieces cemented with CPC-Chem and four kinds of powders (tricalcium phosphate, TCP; magnesium phosphate, MgP; calcium carbonate, CC and magnesium carbonate, MgC) as seed crystals. The UCS of the CPC-Chem test pieces cemented with TCP and CC was significantly greater than that of the test pieces with no added powders. 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 kPa and 209.7 kPa for the test pieces with TCP and CC additives, respectively. Furthermore, the UCS of test pieces with 1 wt% or 5 wt% TCP and 1 wt% CC additives was maintained at a level exceeding 200 kPa for 168 days. SEM observations revealed net-like and three-dimensional structures in segments of test pieces cemented with 1 wt% or 5 wt% TCP and 1 wt% CC in CPC-Chem, which could have been the reason of the long-term stability of UCS (over 200 kPa for 168 days) observed in this study. These results suggest that the addition of TCP and CC significantly enhances the ground improvement afforded by CPC-Chem.
© 2013 The Japanese Geotechnical Society. Production and hosting by Elsevier B.V. All rights reserved.

1. Introduction

Cement-based hardeners are commonly used for ground improvement and play an important role as countermeasures against disasters, including ground liquefaction during an earthquake (Karol, 2003). However, hardener usage involves several environmental problems: large CO_2 emissions during cement production, potential elution of hexavalent chromium from the improved ground, high energy costs for re-excavation of the improved ground, and difficulty in recycling the cement-hardened ground. Recent years have seen the development of a new geotechnical method that involves the use of microorganisms or enzyme for ground permeability control and ground reinforcement (e.g., Whiffin et al., 2007; De Muynck et al., 2010; DeJong et al., 2010; Kawasaki et al., 2010; Stabnikov et al., 2011; Fukue et al., 2011; Al Qabany et al., 2012; Yasuhara et al., 2012). The process of ground improvement by biological action is called "biogrouting" (Van Paassen et al., 2009). A number of mineral formation mechanisms have primarily been considered for biogrout: $CaCO_3$ precipitation using urea and ureolytic bacteria (Harkes et al., 2010); $CaCO_3$ precipitation using glucose and yeast (Kawasaki et al., 2006); siloxane bond formation using

*Corresponding author. Tel./fax: +81 11 706 6318.
E-mail address: kawasaki@geo-er.eng.hokudai.ac.jp (S. Kawasaki).
Peer review under responsibility of The Japanese Geotechnical Society.

This study

Experiment using
chemical reaction

(Akiyama and Kawasaki, 2012a)

Improvement using seed crystal

Experiment using
chemical reaction and microbial activity

(Akiyama and Kawasaki, 2012b)

Experiment using
chemical reaction and microbial activity

Scale up of in vitro experiment

Practical scale experiment

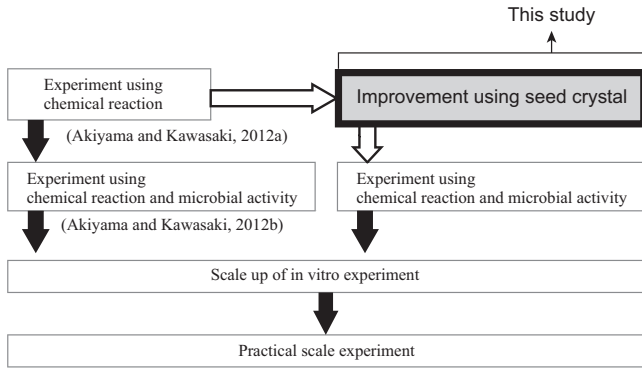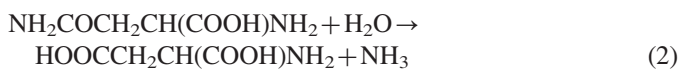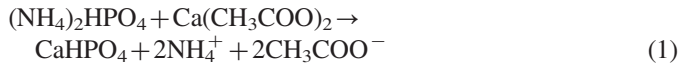Fig. 1. Flowchart of the study. The steps carried out in this study are highlighted in gray.

glucose and yeast (Terajima et al., 2009); and iron- or manganese-compound precipitation using iron-oxidizing bacteria (Weaver et al., 2011). We previously developed a novel ground stabilizer to increase the usage options for cement materials and cementing mechanisms using microorganisms (Fig. 1; Akiyama and Kawasaki, 2012a; Akiyama and Kawasaki, 2012b).

We reported on a calcium phosphate compound (CPC) chemical grout (CPC-Chem, e.g., Eq. (1); Akiyama and Kawasaki, 2012a) that utilizes self-setting CPC mechanisms (Tung, 1998) and on a CPC biogrout (CPC-Bio, e.g., Eq. (2); Akiyama and Kawasaki, 2012b) whose solubility is dependent on its pH (Tung, 1998); this pH can be increased by a microbial reaction (e.g., Eq. (2)).

$$(NH_4)_2HPO_4 + Ca(CH_3COO)_2 \rightarrow$$
$$CaHPO_4 + 2NH_4^+ + 2CH_3COO^- \qquad (1)$$

$$NH_2COCH_2CH(COOH)NH_2 + H_2O \rightarrow$$
$$HOOCCH_2CH(COOH)NH_2 + NH_3 \qquad (2)$$

CPC-Chem has many practical advantages for engineering applications. For example, it is made from agricultural fertilizers and so is easy to obtain and handle, non-toxic, and can be recycled in the form of a fertilizer or re-extracted grout solution. In our previous report, the maximum unconfined compressive strength (UCS) of sand test pieces cemented with CPC-Chem was found to be 63.5 kPa, although the maximum UCS depended on test conditions such as the chemical composition and the curing time of sand test pieces (Akiyama and Kawasaki, 2012a). When CPC-Chem was converted to CPC-Bio by the addition of microorganisms and an ammonia source, the UCS increased from 42.9 kPa to 57.6 kPa (Akiyama and Kawasaki, 2012b). Our aim was to achieve a UCS value of 100 kPa, which is needed to avoid ground liquefaction during earthquakes (Yamazaki et al., 1998). This implies that the UCS of both CPC-Chem and CPC-Bio is sufficient to enable their use as a ground stabilizer, although a further increase in UCS is preferable. However, because these UCS values were obtained in laboratory tests on sand test pieces that were tamped homogeneously, CPC-Chem and CPC-Bio should be strengthened when used as ground stabilizers in a practical setting owing to the complex and heterogeneous ground.

In the medical and dental science fields, CPC paste is used to supplement a lack of bone and teeth through a mechanism called hydroxyapatite (HA, $Ca_5(PO_4)_3OH$) precipitation, which occurs when tetracalcium phosphate (TTCP, $Ca_4(PO_4)_2O$) or dicalcium phosphate (DCP, $CaHPO_4$) is hardened (Chow, 1991). The two CPC powders appear to play two roles during solidification of the paste: as sources of phosphate and calcium for HA and as seed crystals that promote the precipitation and growth of HA (Nancollas and Wefel, 1976; De Rooij et al., 1984; Changsheng and Shen, 1997; Moriyama et al., 2001). The existing biogrout also uses bacterial cells as a nucleus of calcium carbonate precipitation (De Muynck et al., 2010). The oversaturated solution and seed crystals generally coexist to yield effective crystal growth (Miyazaki et al., 2008). These features indicate that the presence of seed crystals can improve the speed and efficiency of crystal precipitation.

In the present study, our aim was to improve CPC-Chem by using two kinds of phosphate powders (tricalcium phosphate, TCP; magnesium phosphate, MgP) and two kinds of carbonate powders (calcium carbonate, CC; magnesium carbonate, MgC) as seed crystals for CPC precipitation. Our goal was to exceed the maximum UCS of 100 kPa, which is the strength required to use a CPC-Chem and powder combination as a countermeasure against ground liquefaction during earthquakes. 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, variation in wet density (ρ_t), and crystal form on the UCS.

2. Selection of powders as seed crystals for CPC precipitation

Table 1 lists the four powders used as seed crystals for CPC precipitation in this study. TCP was chosen from various CPCs (Table 2) because it has two properties that are expected to increase the UCS of the test pieces: the entire precipitation mass can be increased, and TCP can be solidified by a self-setting process. Although CPCs other than TCP can transform into HA through hydrolysis (Table 2), they may significantly

Table 1
Powders used in this study.

Compound	Abbreviation	Established price (JPY/ 500 g)	CAS no.	Mean diameter (μm)	Density (g/cm³)
Tricalcium phosphate $Ca_3(PO_4)_2$	TCP	2800	7758-87-4	12.0	3.14
Magnesium phosphate $Mg_3(PO_4)_2$	MgP	3200	13446-23-6	8.2	2.19
Calcium carbonate $CaCO_3$	CC	2500	471-34-1	17.1	2.93
Magnesium carbonate $MgCO_3$	MgC	2900	56378-72-4	20.7	2.16

Table 2
Hydrolysis of calcium phosphate compounds.

Compound	Ca/P	Abbreviation	Hydrolysis
Monocalcium phosphate	0.5	MCP	$5Ca(H_2PO_4)_2 \cdot H_2O \rightarrow Ca_5(PO_4)_3OH + 7H_3PO_4 + 4H_2O$
Dicalcium phosphate	1.0	DCP	$5CaHPO_4 + H_2O \rightarrow Ca_5(PO_4)_3OH + 2H_3PO_4$
Octacalcium phosphate	1.33	OCP	$5Ca_8(PO_4)_6H_2 \cdot 5H_2O \rightarrow 8Ca_5(PO_4)_3OH + 6H_3PO_4 + 17H_2O$
Tricalcium phosphate	1.5	TCP	$5Ca_3(PO_4)_2 + 3H_2O \rightarrow 3Ca_5(PO_4)_3OH + H_3PO_4$
Hydroxyapatite	1.67	HA	$Ca_5(PO_4)_3OH$
Tetracalcium phosphate	2.0	TTCP	$3Ca_4(PO_4)_2O + 3H_2O \rightarrow 2Ca_5(PO_4)_3OH + 2Ca(OH)_2$

decrease the pH via the release of phosphate ions as a byproduct (Chow, 1991). The low pH induces the dissolution of HA to decrease the CPC precipitation mass and therefore decrease the UCS (Tung, 1998). We chose TCP powder as a seed crystal in part because it releases the lowest amount of phosphate ions during hydrolysis. TCP possesses insolubility in the neutral to weakly alkaline pH range (Tung, 1998), and it is not vulnerable to long-term contact with water because it changes into HA over time by self-setting (Tung, 1998). TCP is an approved food additive in Japan, so it is non-toxic and easy to acquire.

TTCP is also promising as a seed crystal because it releases calcium hydroxide during hydrolysis and does not dissolve the precipitated CPC. However, TTCP is much more expensive than TCP—TTCP costs 420 JPY/g, whereas TCP costs 5.6 JPY/g (Chemicals, 2010)—so we chose to use TCP instead of TTCP in our study. However, from a practical engineering viewpoint, TCP is still too expensive for widespread use. A high-grade reagent was used to fabricate the TCP used in this study; future examination to decrease the cost of the TCP powder is warranted. Although there is little production of TCP at present, the cost of TCP will decrease with increased production in the future.

We also added MgP to the test pieces because it has two potential solidification characteristics, as described below. Precipitated MgP has been used as a quick hardener for the emergency repair of roads and airport runways (Seehra et al., 1993; Mestres and Ginebra, 2011). In addition, MgP and ammonium ions unite to form magnesium ammonium phosphate (struvite, $NH_4MgPO_4 \cdot 6H_2O$), as shown in Eq. (3) (Hagino and Hirajima, 2005).

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow NH_4MgPO_4 \cdot 6H_2O \qquad (3)$$
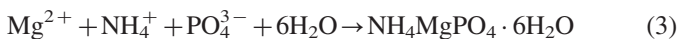
Because the stock solution for CPC-Chem used in this study has ammonium ions as a component, struvite may have been synthesized among the sand particles. The above two facts indicate the possibility of improving the UCS of the sand test pieces by MgP-induced and/or struvite-induced solidification with CPC.

We also used two kinds of carbonate powders: CC and MgC. Previous research on CPC paste has shown that the compressive strength of a mixed paste of DCP and α-tricalcium phosphate can be increased from 35 MPa to a maximum of 56 MPa by using calcium carbonate (CC) as the

seed crystal (Fernández et al., 1998). This observation indicates that the presence 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 oyster and scallop shells, which are disposed of in large quantities as marine industrial waste (410,000 t/year in Japan; Ports and Harbors Bureau, 2004). Moreover, CC is the main component of limestone, and it is non-toxic and inexpensive. Therefore, CC is a promising material in the geotechnical field in terms of waste utilization and cost effectiveness.

The carbonate MgC has also been used as a main contributor to solidification in soil hardeners after precipitation (Fujimori and Kobori, 2000). Magnesite ($MgCO_3$) and dolomite ($CaMg(CO_3)_2$), which are Mg-containing carbonates, have a lower solubility than CC (Chou et al., 2000). Thus, improved strength and chemical stability in the ground can be expected when MgC and CPC-Chem are used. MgC is also non-toxic and recyclable, as are the previous three powders.

A comparison of phosphate–carbonate and/or calcium–magnesium may be useful to understanding the contribution of each component to sand solidification. Physical improvement of the strength of the test pieces is also expected because smaller powders fill up the spaces between the sand particles and induce an increase in density.

Thus, we used TCP, MgP, CC, and MgC as promising candidates for seed crystals to improve ground solidification.

3. Materials and methods

The CPC-Chem used in this study was a 1.5:0.75 M mixture of diammonium phosphate (DAP) and calcium acetate (CA). We used this mixture because it was previously reported to yield the highest UCS among all combination ratios of DAP with calcium nitrate or CA (Akiyama and Kawasaki, 2012a).

A standard sand test piece was made from 320.09 g of Toyoura sand (soil particle density $\rho_s = 2.64$ g/cm^3, minimum density $\rho_{min} = 1.335$ g/cm^3, maximum density $\rho_{max} = 1.645$ g/cm^3, mean diameter $D_{50} = 170$ μm) and 73.3 mL of CPC-Chem (density $\rho_c = 1.16$ g/cm^3) following a previous report (Akiyama and Kawasaki, 2012a). The test pieces were made with the weight combination ratios of sand, powder, and additive of CPC-Chem and deionized water as shown in Fig. 2. First, 1% (3.2 g, denoted as Powder-01), 5% (16.0 g, denoted as Powder-05), and 10% (32.0 g, denoted as Powder-10) of powder were added to 316.89,

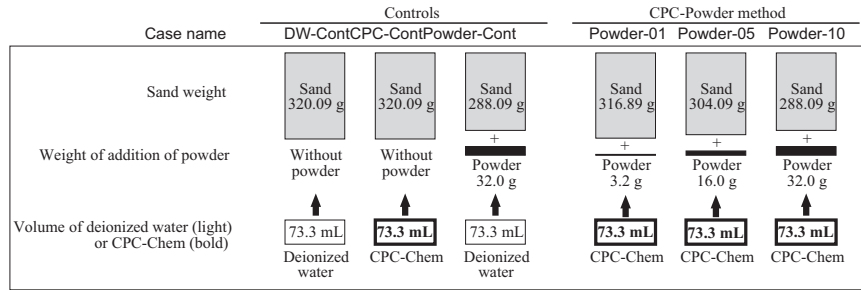| Case name	Controls			CPC-Powder method		
	DW-Cont	CPC-Cont	Powder-Cont	Powder-01	Powder-05	Powder-10
Sand weight	Sand 320.09 g	Sand 320.09 g	Sand 288.09 g	Sand 316.89 g	Sand 304.09 g	Sand 288.09 g
Weight of addition of powder	Without powder	Without powder	+ Powder 32.0 g	+ Powder 3.2 g	+ Powder 16.0 g	+ Powder 32.0 g
Volume of deionized water (light) or CPC-Chem (bold)	73.3 mL Deionized water	**73.3 mL** CPC-Chem	73.3 mL Deionized water	**73.3 mL** CPC-Chem	**73.3 mL** CPC-Chem	**73.3 mL** CPC-Chem

Fig. 2. Conceptual image of making test pieces.

304.09, and 288.09 g, respectively, of Toyoura sand; each time, they yielded a standard sand test piece weight of 320.09 g. Next, CPC-Chem was added to the mixture of sand and powder. The mixture was uniformly mixed in a stainless steel ball for 2 and then divided into quarters. Each quarter was then placed into a plastic mold (inner diameter $\varphi = 5$ cm, height $h = 10$ cm). To avoid disturbing the test pieces during their removal from the mold, the inner wall of each mold was covered with a 0.1-mm-thick overhead projector sheet. After each of the four quarters was placed in the mold, the mixture was tamped down 30 times by a hand rammer. Finally, the upper edges of the test pieces were slightly trimmed to be flat and covered with Parafilm M (Structure Probe, Inc., West Chester, PA) to avoid desiccation. The molded test pieces that were wet with CPC-Chem or deionized water were subsequently cured in an airtight container at a high humidity at 20 °C. Hereafter, the method of improving ground strength by adding a powder to CPC-Chem is referred to as the CPC-Powder method and each experimental case is named by combining the corresponding weight ratio with the kind of powder used (e.g., CPC-Chem with 1 wt% TCP is denoted as TCP-01). The control samples were cemented with deionized water only (DW-Cont), CPC-Chem only (CPC-Cont), and deionized water and powder (TCP-Cont, MgP-Cont, CC-Cont, and MgC-Cont). Five of the six controls, excluding CPC-Cont, were cured for 28 days. The CPC-Cont, MgP-01–MgP-10, and MgC-01–MgC-10 samples were cured for 1, 14, and 28 days. The curing times for the TCP-01–TCP-10 and CC-01–CC-10 samples were 1, 14, 28, 56, and 168 days. The UCS of the test pieces removed from the mold after curing was measured with a UCS apparatus T266-31100 (Seiken-sha Co., Ltd., Japan) at an axial strain rate of 1%/min. One test piece from each of the DW-Cont, TCP-Cont, MgP-Cont, CC-Cont, and MgC-Cont samples was examined by the UCS test. For the other cases, two test pieces were measured. The pH of the test pieces was calculated as an average of three measurements (top, bottom, and middle of each test piece) using a pH Spear (Eutech Instruments Pte., Ltd., Singapore). This pH device was designed to measure the pH of solids and semisolids, including gels (e.g., Wilson et al., 2010).

Segments of the UCS test pieces were observed by SEM (SuperScan SS-550, Shimadzu Corporation, Kyoto). The segments were naturally dried at 20 °C for a few days and coated with a carbon coater (Quick Carbon Coater SC-701C, Sanyu Electron Co., Ltd., Tokyo). SEM observations were carried out at an accelerating voltage of 15 kV and magnification of 2000 ×.

4. Results and discussion

4.1. Stress–strain curves

For each test case, we selected the test piece with the largest UCS. The stress (σ)–strain (ε) curves of these selected samples are shown in Fig. 3. The two stress–strain curves obtained for each test case showed almost the same behavior in terms of shape. All of the stress–strain curves of the TCP-added test pieces (Fig. 3a, bold lines) after 28 days had a higher peak and smaller failure strain (ε_f) of around 1.0% compared with the MgP-added test pieces (Fig. 3a, light lines). The TCP-01 and TCP-05 samples after 168 days had stress–strain curves similar to those after 28 days, while the TCP-10 sample after 168 days had a slightly larger failure strain than that after 28 days (Fig. 3b). The CC-added test pieces had clear peaks on the stress–strain curve after 28 and 168 days, but the failure strains were dispersed from 0.5% to 2.0% (Fig. 3c and d). For the stress–strain curve of the CC-01 sample, there was no significant difference between the curves after 28 days and after 168 days. The failure strain of the MgP- and MgC-added test pieces showed relative ranges of 0.5%–1.7% and 0.5%–1.0%, respectively.

The stress–strain curves of the DW-Cont, TCP-Cont, MgP-Cont, CC-Cont, and MgC-Cont samples could not be obtained because these five control samples did not include cement materials and fractured owing to their self-weight. This confirmed that TCP, MgP, CC, and MgC do not possess pozzolanic properties.

4.2. pH of test pieces

For the six control samples, the pH of the test pieces ranged from neutral to weakly alkaline, while the addition of TCP resulted in a weakly acidic (6.0–6.5) pH (Fig. 4). When MgP was added, all of the test pieces showed acidic values of pH; for the MgP-10 sample in particular, the pH value after one day was 3.7. The pH values for the CC and MgC samples, which are carbonates, exceeded 7.

4.3. SEM observation

Figs. 5 and 6 show SEM images of five of the six control samples and those of the test pieces made by the CPC-Powder method, respectively.
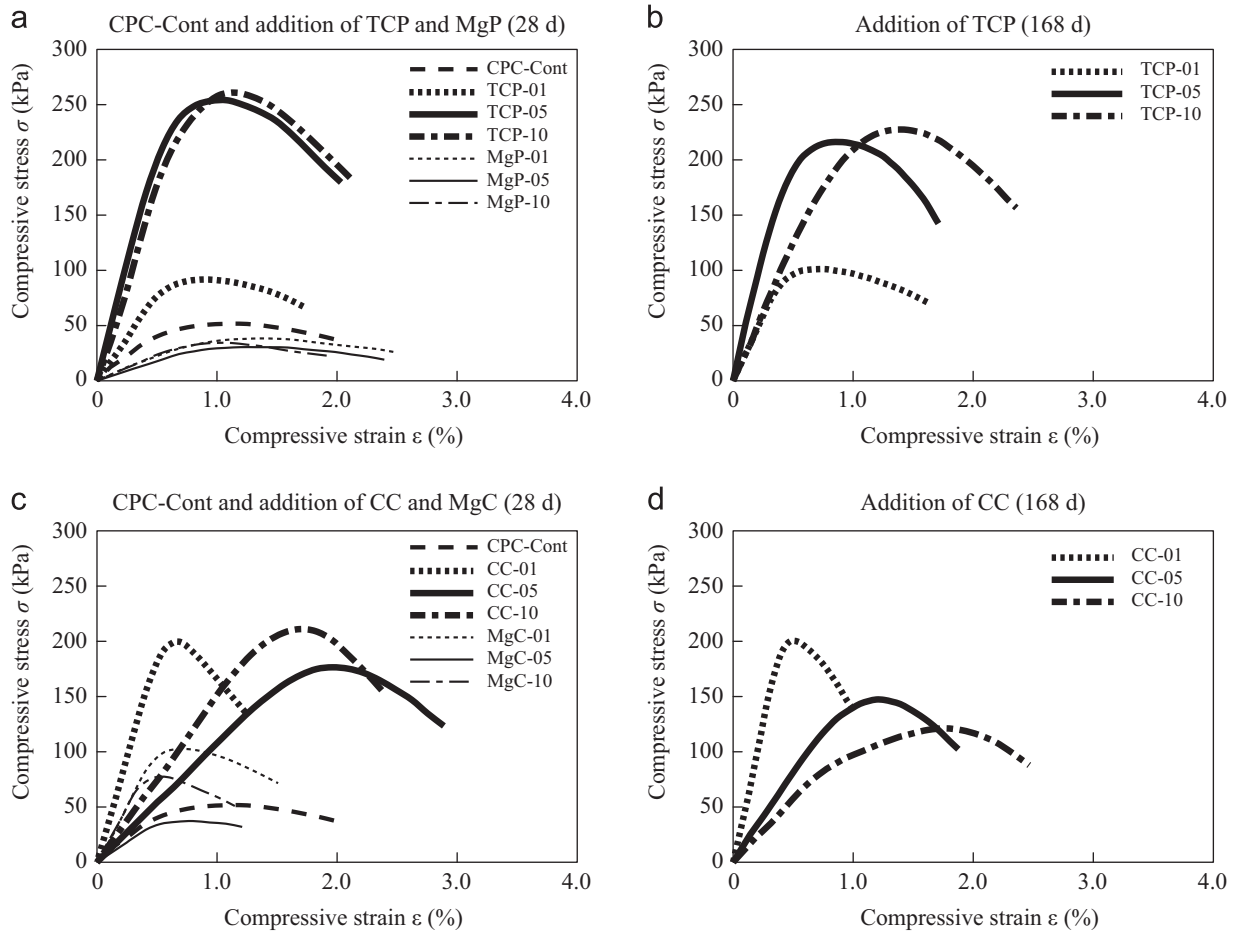
Fig. 3. Stress–strain curves. (a) CPC-Cont and addition of TCP and MgP (28 days), (b) Addition of TCP (168 days), (c)CPC-Cont and addition of CC and MgC (28 days) and (d) Addition of CC (168 days). (Only the highest UCS values are shown in each case).
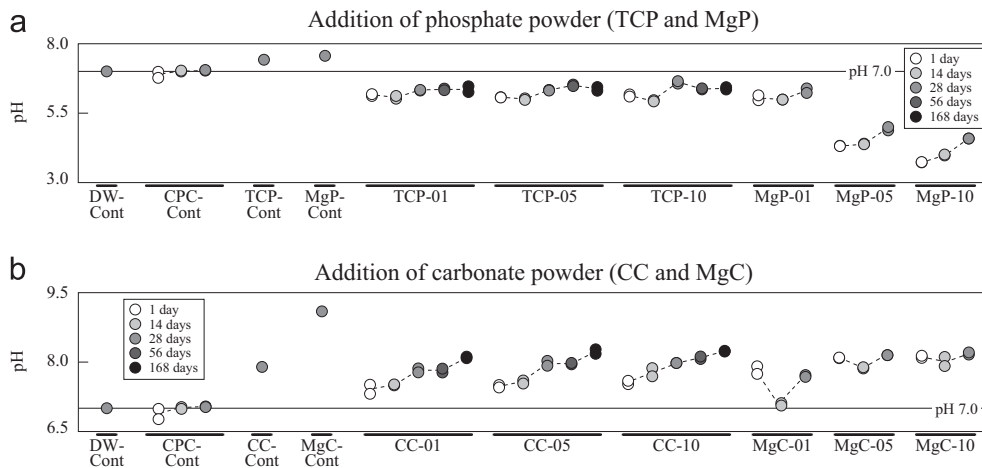

Fig. 4. Temporal variations in the pH of the test pieces. (a) Addition of phosphate powder (TCP and MgP) and (b) Addition of carbonate powder (CC and MgC). (The data for CPC-Cont are drawn in both (a) and (b) for convenience of comparison).

Whisker-like or fiber-like crystals in the CPC-Cont sample (Fig. 5e) and cuboid-like crystals in the CC-Cont sample (Fig. 5c) were observed. Such structures were not observed in the other control samples; the SEM images showed only powder aggregation attached to the surface of the sand particles. SEM

images showed that the precipitation of TCP-01 after 28 (Fig. 6a) and 168 days (Fig. 6b) and TCP-05 after 28 days (Fig. 6c) had net-like and three-dimensional (3D) structures; the precipitation of TCP-05 after 168 days (Fig. 6d) and TCP-10 after 28 (Fig. 6e) and 168 days (Fig. 6f) had 1-μm-diameter
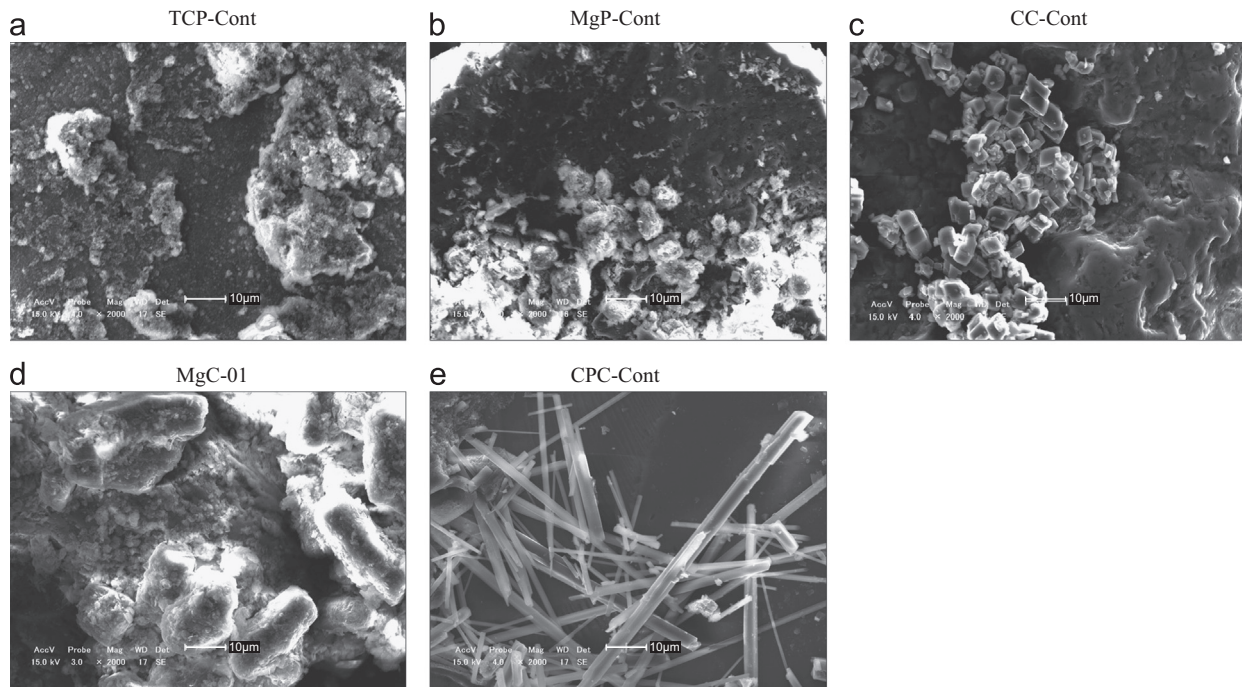
Fig. 5. SEM images of test pieces for the five control samples after 28 days (2000 ×). (a) TCP-Cont, (b) MgP-Cont, (c) CC-Cont, (d) MgC-01 and (e) CPC-Cont.

particle-like crystals instead of net-like crystals, and the particles filled up the spaces between the whisker-like crystals.

For the MgP-01 sample, numerous 10-μm-long crystals were observed (Fig. 6g). In the MgP-05 sample, 1–5-μm-diameter small crystals on the surface of the sand particles were observed (Fig. 6h). For the MgP-10 sample, many aggregations of plate-like crystals over 10 μm in length were observed (Fig. 6i).

SEM images of the CPC-CC samples (i.e., CC-01, CC-05, and CC-10) did not show whisker-like structures as observed for the CPC-Cont sample; the images did not even show cuboid-like structures as observed for the CC-Cont sample. Instead, CC-01 (Fig. 6j and k) had net-like 3D structures, and CC-05 and CC-10 had unified structures of sand particles and CPC precipitation (Fig. 6l–o). Similar to MgP, numerous 10-μm-long crystals were observed in the case of MgC (Fig. 6p–r) without any unification with sand particles.

4.4. Effect of addition of TCP and CC on the UCS of test pieces

Fig. 7 shows the UCS test results. The UCS of test pieces cemented with CPC-Chem and TCP or CC was larger than that for CPC-Chem alone, and it increased with time (Fig. 7). For the TCP-05 and TCP-10 samples in particular, the UCS was around 150 kPa after 1 day; it exceeded 250 kPa after 28 days and remained at about 200 kPa even after 168 days. The UCS of the CC-01 sample also increased from about 100 kPa to 200 kPa and it remained at that level. Although the UCS of the CC-05 and CC-10 samples showed an increasing trend over 56 days, the UCS thereafter decreased to below 150 kPa. To clarify the reason for the decrease in UCS over time for some

test pieces, further examination of the long-term strength of test pieces in the CPC-Powder method is needed in the future.

SEM observation showed net-like 3D structures in TCP-01 and TCP-05 and whisker-like crystals in TCP-10. In our previous report (Akiyama and Kawasaki, 2012a), the test sample that showed the highest UCS value had a whisker-like crystal structure, which is consistent with the results of this study. In addition, those whisker-like crystals developed 3D structures, which seems to be one of the reasons for the significant improvement in the UCS. The failure strain of the TCP-added test pieces ranged from 0.5% to 1.5% independent of the UCS. These results suggest that the 3D and whisker-like structures demonstrated brittle behavior in the test pieces and demonstrate the necessity of clarifying how the strength and deformation properties of the test pieces cemented with the CPC-Powder method would apply to actual ground conditions.

Almost all of the test pieces to which the CC powder was added showed a UCS larger than 100 kPa. This observation suggests that through control of the CC content, the 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, because the upper face of the test pieces cemented with CC powder and CPC-Chem covered with Parafilm swelled somewhat immediately after the mixing of materials, the strength may be improved by the addition of vertical confining pressure. This means that ground improvements made with CPC-Chem and CC powder can be utilized in subsurface environments where triaxial confining pressure occurs.

CC-01 had a net-like 3D structure in which the precipitated CPC that enveloped the CC particles bonded with the surface of the sand particles. Such bonding was also observed in CC-05 and CC-10 but without the formation of any crystal structure. The
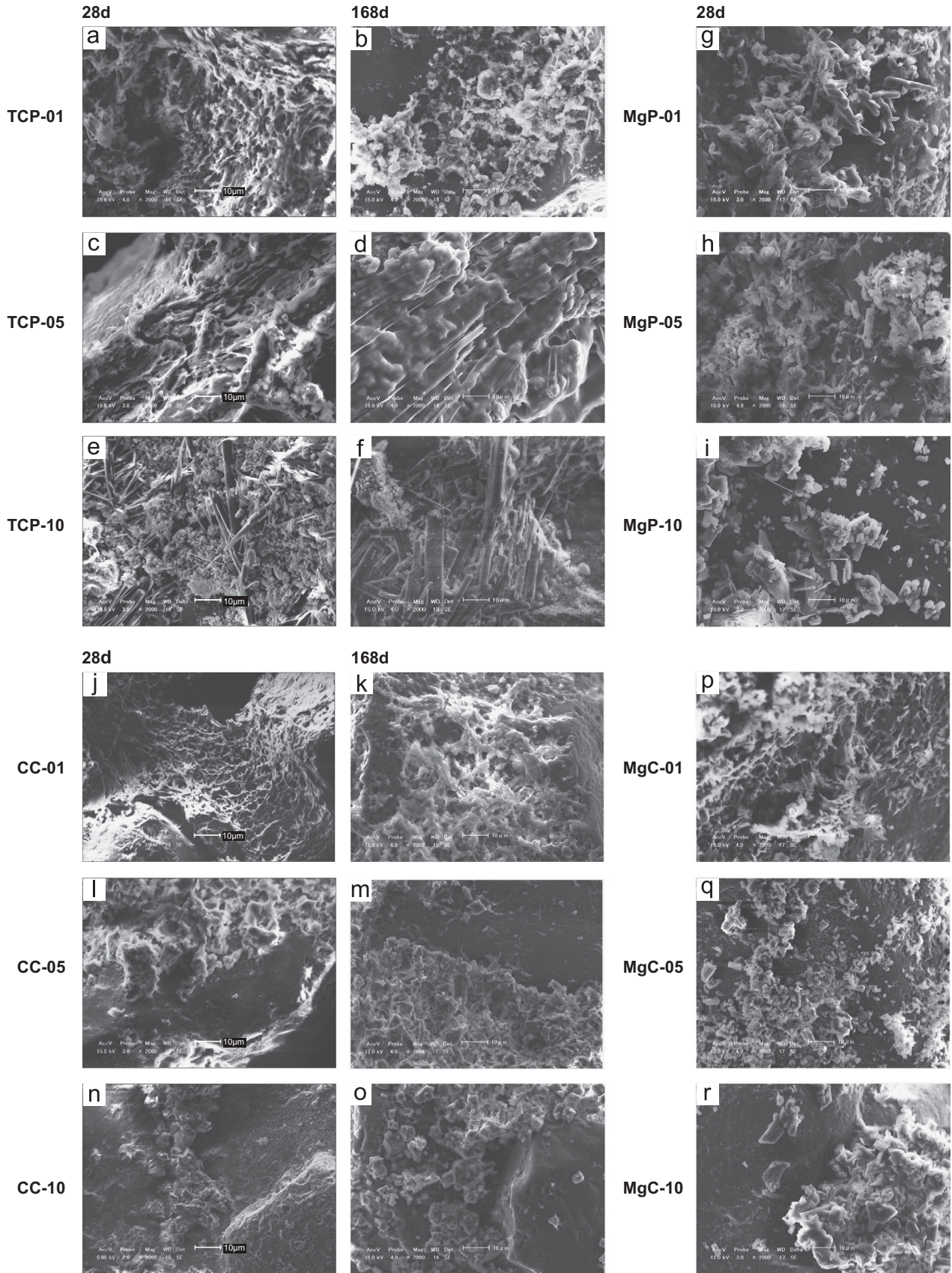
28d   **168d**   **28d**

TCP-01

TCP-05

TCP-10

MgP-01

MgP-05

MgP-10

28d   **168d**

CC-01

CC-05

CC-10

MgC-01

MgC-05

MgC-10

Fig. 6. SEM images of test pieces 28 days (TCP, MgP, CC, and MgC) and 168 days (TCP and CC) (2000 ×) after they were cemented with the CPC-Powder Method.
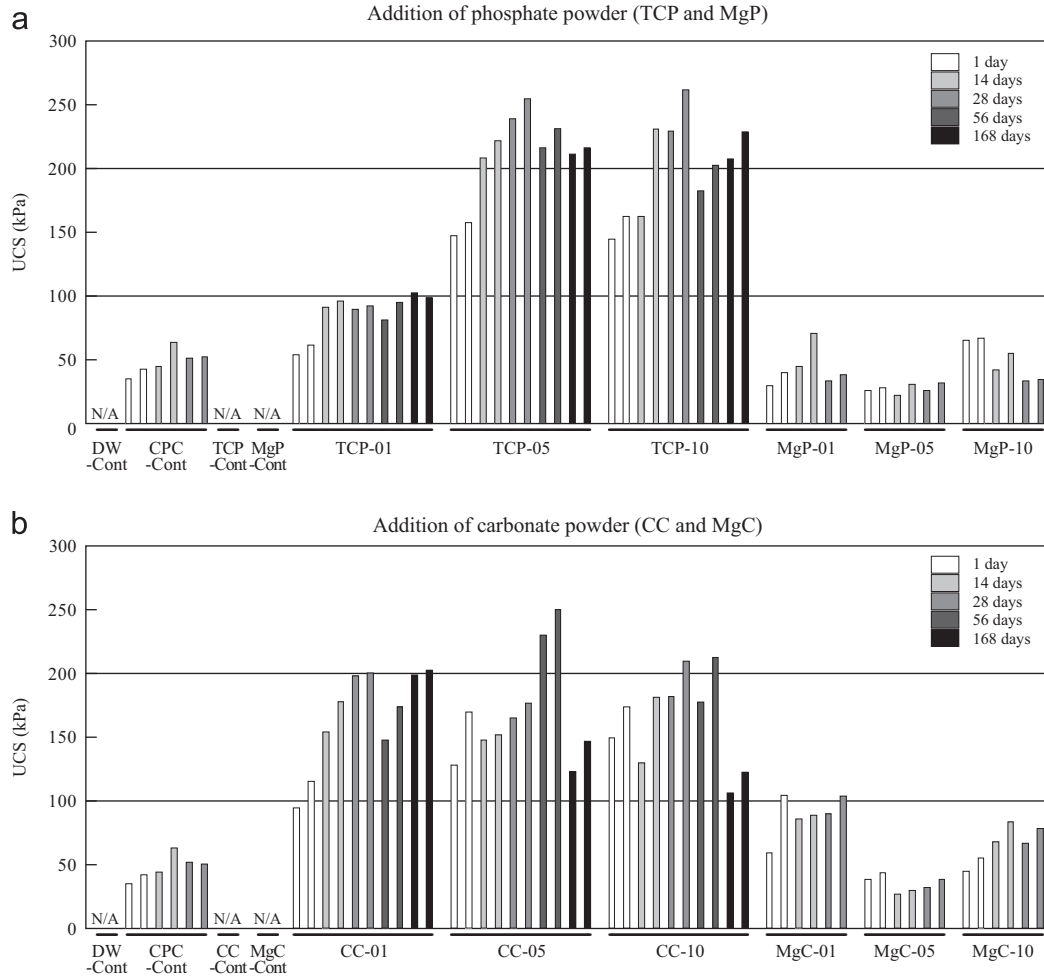
Fig. 7. Temporal variations in the UCS of the test pieces. (a) Addition of phosphate powder (TCP and MgP) and (b) Addition of carbonate powder (CC and MgC). (The data for CPC-Cont are drawn in both (a) and (b) for convenience of comparison).

difference between the failure strain of CC-01 (Fig. 3), with its net-like structure (Fig. 6j and k), and that of CC-05/CC-10, which did not show any crystal structure (Fig. 6l–o), suggests that the crystal structure of the CPC-CC in the sand test pieces affects the strength/deformation properties of the test pieces.

The pH values of the test pieces with added TCP and CC were weakly acidic, with a value below 7 and weakly alkaline with a value below 8, respectively. Because the solubility of CPC is lower under weak alkaline conditions (Tung, 1998), we can utilize the mechanism of CPC-Bio (Akiyama and Kawasaki, 2012b) to increase the CPC precipitation. This is achieved by using micro-organisms and ammonia sources to increase the pH to 9 via a pH-increasing reaction and would result in a further increase in the UCS. In a future study, we intend to report on the effect of CC addition on the UCS of sand test pieces cemented with CPC-Bio.

4.5. Effect of addition of MgP and MgC on the UCS of test pieces

For the cases in which magnesium compounds (MgP and MgC) were added, all the test pieces except for MgC-01 showed a UCS similar to or lower than that with the CPC-Cont control sample (Fig. 7). This result shows that the addition of

magnesium compounds is not effective for ground improvement using CPC-Chem. The release of magnesium ions from the magnesium compounds is considered to be an inhibiting factor on the self-setting of CPC (Amjad et al., 1984; Salimi et al., 1985; Kibalczyc et al., 1990; Campbell et al., 1991). In this study, CPC precipitation was induced by mixing a phosphate stock solution and calcium stock solution, both of which had relatively high ion concentrations (Tung, 1998). Considering the high concentrations of the stock solutions, a gradual variation from an amorphous or gel-like CPC to HA was assumed to occur. This indicates that the magnesium ions isolated from the magnesium compounds immediately after mixing of the stock solutions were exchanged with the calcium ions or taken into the crystal structure during the self-setting process to HA, which decreased the UCS. On the other hand, the SEM images showed that numerous small crystals, which were thought to be a magnesium compound (MgP or MgC), were present without unifying with the sand particles. This result suggests that struvite and Mg-containing carbonates such as magnesite and dolomite were not synthesized in this study.

The above results indicate that magnesium compounds and CPC-Chem did not have a multiplier effect on ground improvement under the conditions of this study.
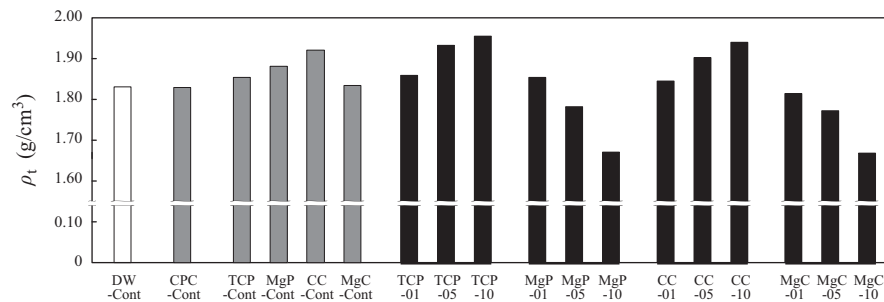
Fig. 8. Wet density of test pieces.

4.6. Effect of wet density and precipitation amount on UCS

Fig. 8 shows the initial wet density of the test pieces. Immediately after being produced and cured, the wet densities of two test pieces in each test case showed almost the same value. We expected an increase in density through the addition of less powder than sand particles, which should result in an improved UCS. As shown in Fig. 8, the wet density of the test pieces cemented by TCP and CC powders with CPC-Chem increased with the amount of added powder, whereas the wet density when MgP and MgC were added decreased with an increase in powder addition and showed a smaller value than that of the DW-Cont control. The differences in wet density between calcium compounds and magnesium compounds may be explained by the differences in density of the powders themselves (TCP and CC, about 3 g/cm^3; MgP and MgC, about 2.2 g/cm^3) and the crystal growth pressure of other magnesium compounds by the addition of MgP and MgC (Chatterji, 2005).

When the UCS values were compared based on the amount of powder added, TCP-05 had a UCS similar to that of TCP-10, there was a significant difference in the UCS among the three kinds of CC addition, and the addition of a 5 wt% magnesium compound induced the lowest UCS of the three additive amounts for each magnesium compound. These results suggest a clear relation between the amount of powder added and UCS and that the addition of TCP does not significantly contribute to the wet density and improvement in UCS.

The UCS has been reported to increase with the ratio of the cement material mass to the mass of the particles of the base material (Kobayashi and Tatsuoka, 1982; Molenaar and Venmans, 1993). In the present study, the weight ratios (%) of the cement material (i.e., additional powder and CPC precipitated from CPC-Chem) relative to the entire weight of the test piece were 2.7% for a 1 wt% addition, 6.6% for a 5 wt% addition, and 11.5% for a 10 wt% addition. These ratios were calculated from the volume, wet density, amount of additional powder, and theoretical weight of the CPC precipitated from CPC-Chem (5.5 g, Akiyama and Kawasaki, 2012a). However, as in the case of the wet density, the UCS of the test pieces did not increase with the cement material mass.

As noted above, the UCS clearly increased with the ratio of cement to base material if the amount of base material in each

test piece was consistent or almost the same. However, the test results indicated that the mass of base sand material in each test piece decreased according to the amount of powder added. In other words, the void ratio of the base sand structure increased as more powder was added. This aspect should be considered when examining why the UCS did not increase with the cement material mass. To clarify the effect of the amounts of added powder, precipitated CPC, and base material on the UCS, variations in the amount of powder added in the CPC-Powder method need to be investigated.

4.7. Applicability of CPC-Powder method

In this study, we showed that CPC-Chem 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 261.4 kPa and exhibited long-term stability of over 200 kPa. Next, we discuss the application prospects based on the merits and mechanical properties.

The CPC-Powder method can be applied to producing columns in soft ground as a sand compaction pile method or deep mixing method. In the sand compaction pile method, sand is pumped and installed as a column into soft ground, which is the same situation as that for the DW-Cont sample in this study. This means that ground improvement using the CPC-Powder method may be capable of achieving a UCS of 261.4 kPa in comparison to the negligible UCS of sand or DW-Cont alone.

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 200 kPa. This makes the CPC-TCP or CPC-CC method promising for some concrete applications, which are as follows. First, sludge from construction sites can be reused as soil material because a cone index (q_c) of over 800 kPa, which corresponds to a UCS of over 160 kPa, is recommended for reusable sludge (Japanese Geotechnical Society, 2000). Next, backfill soil can be reinforced. Because of ground liquefaction during earthquakes, backfill soil tends to subside and manholes and pipelines in the soil tend to be pushed upward; this causes substantial damage to the infrastructure. Hence, backfill soil must be reinforced as a countermeasure against such an occurrence. The Public Works

Research Institute (2008) suggests that a UCS of 100–200 kPa is required for backfill soil reinforcement. The UCS attained by the addition of TCP and CC powder as shown in this study satisfies this requirement. Furthermore, unlike ground treated with cement-based hardeners, ground treated with the CPC-Powder method can be re-excavated and recycled. This means that the CPC-Powder method can be used as a temporary supplemental hardening method. We are planning to conduct a practical-scale experiment in actual ground.

5. Conclusions

In order to improve the performance of CPC-Chem, we conducted UCS tests on test pieces cemented with a combination of CPC-Chem and various powders. The results confirmed that the addition of powder increases the UCS of the test pieces and may be applied to CPC-Bio as follows:

(1) The UCS of test pieces cemented with CPC-Chem and calcium compound (TCP and CC) powders significantly increased compared to cases where no powder was added to CPC-Chem. In particular, TCP-05, TCP-10, and CC-01 maintained a stable UCS of around 200 kPa for 168 days.
(2) In the test pieces cemented with CPC-Chem and magnesium compounds (MgP and MgC), the UCS was not much larger or was a little smaller than that for CPC-Chem alone.
(3) Because the pH of the test pieces cemented with CPC-Chem and TCP powder was below 7 and that of the test pieces cemented with CPC-Chem and CC powder was below 8, the strength can be further increased by a pH-increasing reaction to pH 9 using microbial activity (CPC-Bio).

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 geoenvironmental engineering.

References

Akiyama, M., Kawasaki, S., 2012a. Novel grout material using calcium phosphate compounds: in vitro evaluation of crystal precipitation and strength reinforcement. Eng. Geol. 125, 119–128.
Akiyama, M., Kawasaki, S., 2012b. Microbially mediated sand solidification using calcium phosphate compounds. Eng. Geol. 137–138, 29–39.
Al Qabany, A., Soga, K., Santamarina, C., 2012. Factors affecting efficiency of microbially induced calcite precipitation. J. Geotech. Geoenviron. Eng. 138, 992–1001.
Amjad, Z., Koutsoukos, P.G., Nancollas, G.H., 1984. The crystallization of hydroxyapatite and fluorapatite in the presence of magnesium ions. J. Colloid Interface Sci. 101, 250–256.
Campbell, A.A., LoRe, M., Nancollas, G.H., 1991. The influence of carbonate and magnesium ions on the growth of hydroxyapatite, carbonated apatite and human powdered enamel. Colloids Surf. 54, 25–31.
Changsheng, L., Shen, W., 1997. Effect of crystal seeding on the hydration of calcium phosphate cement. J. Mater. Sci. -Mater. M. 8, 803–807.
Chatterji, S., 2005. Aspects of generation of destructive crystal growth pressure. J. Cryst. Growth 277, 566–577.
Chemicals (Ed.) Wako Pure Chemical Industries, Ltd., 36th Edition, 2010.
Chou, L., Garrels, R.M., Wollast, R., 2000. Comparative study of the kinetics and mechanisms of dissolution of carbonate minerals. Chem. Geol. 78, 269–282.
Chow, L.C., 1991. Development of self-setting calcium phosphate cements. Centennial Mem. Issue of Ceram. Soc. Jpn. 99, 954–964.
De Muynck, W., De Belie, N., Verstraete, W., 2010. Microbial carbonate precipitation in construction materials: a review. Ecol. Eng. 36, 118–136.
De Rooij, J.F., Heughebaert, J.C., Nancollas, G.H., 1984. A pH study of calcium phosphate seeded precipitation. J. Colloid Interf. Sci. 100, 350–358.
DeJong, J.T., Mortensen, B.M., Martinez, B.C., Nelson, D.C., 2010. Bio-mediated soil improvement. Ecol. Eng. 36, 197–210.
Fernández, E., Gil, F.J., Best, S.M., Ginebra, M.P., Driessens, F.C.M., Planell, J.A., 1998. Improvement of the mechanical properties of new calcium phosphate bone cements in the $CaHPO_4$-α-$Ca_2(PO_4)_2$ system: compressive strength and microstructural development. J. Biomed. Mater. Res. 41, 560–567.
Fujimori, S., Kobori, S., 2000. Characteristics and available range of soil hardening chemical of Mug White. J. Agric. Eng. Soc. Jpn. 68, 53–56 (in Japanese).
Fukue, M., Ono, S., Sato, Y., 2011. Cementation of sands due to microbiologically-induced carbonate precipitation. Soils Found. 51 (1), 83–93.
Hagino, T., Hirajima, T., 2005. Development of process for recovering phosphorus from sewage sludge. Resour. Process 52, 172–182.
Harkes, M.P., Van Paassen, L.A., Booster, J.L., Whiffin, V.S., Van Loosdrecht, M.C.M., 2010. Fixation and distribution of bacterial activity in sand to induce carbonate precipitation for ground reinforcement. Ecol. Eng. 36, 112–117.
Japanese Geotechnical Society, 2000. Doshitsushiken no Houhou to Kaisetsu, Japanese Geotechnical Society, Tokyo (in Japanese).
Karol, R.H., 2003. Chemical grouting and soil stabilization, 3rd ed. CRC Press, Boca Raton, FL.
Kawasaki, S., Murao, A., Hiroyoshi, N., Tsunekawa, M., Kaneko, K., 2006. Fundamental study on novel grout cementing due to microbial metabolism. J. Jpn. Soc. Eng. Geol. 47, 2–12 (in Japanese with English abstract).
Kawasaki, S., Ogata, S., Hiroyoshi, N., Tsunekawa, M., Kaneko, K., Terajima, R., 2010. Effect of temperature on precipitation of calcium carbonate using soil microorganisms. J. Jpn. Soc. Eng. Geol. 51, 10–18 (in Japanese with English abstract).
Kibalczyc, W., Christoffersen, J., Christoffersen, M.R., Zielenkiewcz, A., Zielenkiewicz, W., 1990. The effect of magnesium ions on the precipitation of calcium phosphates. J. Cryst. Growth 106, 355–366.
Kobayashi, A., Tatsuoka, F., 1982. Mechanical properties of saturated soft clay improved by cement-mixing. Seisan Kenkyu 34, 304–307 (in Japanese).
Mestres, G., Ginebra, M.P., 2011. Novel magnesium phosphate cements with high early strength and antibacterial properties. Acta Biomater. 7, 1853–1861.
Miyazaki, H., Adachi, N, Ota, T., 2008. Crystal growth by solution dropping technique mimicking stalagmite growth in nature. Ann. Rep. Res. Lab., Nagoya Inst. Technol. 8, 13–16 (in Japanese with English abstract).
Molenaar, N., Venmans, A.A.M., 1993. Calcium carbonate cementation of sand: A method for producing artificially cemented samples for geotechnical testing and a comparison with natural cementation processes. Eng. Geol. 35, 103–122.
Moriyama, K., Kojima, T., Minawa, Y., Matsumoto, S., Nakamachi, K., 2001. Development of artificial seed crystal for crystallization of calcium phosphate. Environ. Technol. 22, 1245–1252.
Nancollas, G.H., Wefel, J.S., 1976. Seeded growth of calcium phosphates: Effect of different calcium phosphate seed material. J. Dent. Res. 55, 617–624.
Ports and Harbors Bureau, 2004. ⟨http://www.mlit.go.jp/kowan/recycle/⟩, Recycling technology guidelines for harbor and airport construction and maintenance.
Public Works Research Institute, 2008. Kensetsuodei Saisei Riyou Manual. Taisei Publishing Co., Ltd., Tokyo (in Japanese).

Salimi, M.H., Heughebaert, J.C., Nancollas, G.H., 1985. Crystal growth of calcium phosphates in the presence of magnesium ions. Langmuir 1, 119–122.

Seehra, S.S., Gupta, S., Kumar, S., 1993. Rapid setting magnesium cement for quick repair of concrete pavements – Characterization and durability aspects. Cem. Conc. Res. 23, 254–266.

Stabnikov, V., Naeimi, M., Ivanov, V., Chu, J., 2011. Formation of water-impermeable crust on sand surface using biocement. Cement Concr. Res. 41, 1143–1149.

Terajima, R., Shimada, S., Oyama, T., Kawasaki, S., 2009. Fundamental study of siliceous biogrout for eco-friendly soil improvement. J. Jpn. Soc. Civil. Eng. Ser. C 65, 120–130 (in Japanese with English abstract).

Tung, M.S., 1998. Calcium phosphates: structure, composition, solubility, and stability. In: Zahid, A. (Ed.), Calcium Phosphates in Biological and Industrial Systems. Kluwer Academic Publishers, Norwell, pp. 1–19.

Van Paassen, L.A., Harkes, M.P., Van Zwieten, G.A., Van der Zon, W.H., Van der Star, W.R.L., Van Loosdrecht, M.C.M., 2009. Scale up of biogrout: a biological ground reinforcement method, In: Proceedings of the 17th International Conference on Soil Mechanics and Geotechnical Engineering, pp. 2328–2333.

Weaver, T.J., Burbank, M., Lewis, A., Crawford, R., Williams, B., 2011. Bio-induced calcite, iron, and manganese precipitation for geotechnical engineering applications. Proc. Geo-Frontiers 2011, 3975–3983.

Whiffin, V.S., Van Paassen, L.A., Harkes, M.P., 2007. Microbial carbonate precipitation as a soil improvement technique. Geomicrobiol. J. 24, 417–423.

Wilson, E.E., Yound, C.V., Holway, D.A., 2010. Predation or scavenging? Thoracic muscle pH and rates of water loss reveal cause of death in arthropods. J. Exp. Biol. 213, 2640–2646.

Yamazaki, H., Maeda, K., Takahashi, K., Zen, K., Hayashi, K., 1998. Development of counter-measure against liquefaction by using solution type grout. Tech. Note of Port Harbour Res. Inst. 905, 29 (in Japanese).

Yasuhara, H., Neupane, D., Hayashi, K., Okamura, M., 2012. Experiments and predictions of physical properties of sand cemented by enzymatically-induced carbonate precipitation. Soils Found. 52 (3), 539–549.