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Novel grout material comprised of calcium phosphate compounds: In vitro evaluation of crystal precipitation and strength reinforcement

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ABSTRACT

Calcium phosphate compounds (CPCs) have unique physicochemical properties. As grout material, they afford many advantages such as adequate physical strength, self-setting property, pH dependence of precipitation, non-toxicity, and recyclability. To apply CPCs to the permeability control and reinforcement of ground soil and rock, we explored suitable conditions for in vitro CPC precipitation, conducted unconfined compressive strength (UCS) tests of Toyoura sand test pieces cemented by CPC, and carried out observations and elemental analysis of precipitated CPC crystals. Two kinds of phosphate stock solution and two kinds of calcium stock solution were used to prepare the reaction mixtures, and CPC precipitation was detected in all reaction mixtures. The volume of CPC precipitation in the reaction mixture increased as the pH rose from strongly acidic to around neutral. The UCS of Toyoura 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 63.5 kPa after 14 days of curing. Conversely, the UCS of test pieces cemented by using calcium nitrate was below 20 kPa and showed no significant increase in strength. CPC precipitation with calcium nitrate induced the formation of plate-like crystals, whereas that with calcium acetate induced whisker-like crystals. Elemental analysis of the cemented test pieces showed that the distributions of phosphorus and calcium were similar. The results indicate the practical feasibility of using novel CPC grouts as chemical grouts because of their self-setting property, and as biogrouts because of their crystal structure and pH dependence of precipitation.

1. Introduction

In recent years, grout materials that exploit mechanisms of cement material production by microorganisms have been developed for ground permeability control and reinforcement (Whiffin et al., 2007; de Muynck et al., 2010; DeJong et al., 2010; Harkes et al., 2010; Kawasaki et al., 2010). The process of ground improvement by biological action is called “biogrouting” (van Paassen et al., 2009).

Three mechanisms of mineral formation have mainly been considered for biogrouting. One is the precipitation of calcium carbonate by in situ microorganisms and/or added yeasts (Kawasaki et al., 2006). In this process, calcium carbonate is precipitated by the binding of carbonate ions released from microorganisms and calcium ions from the injected grout, which includes calcium and glucose. A second mechanism was reported by Harkes et al. (2010), who used urea instead of glucose and urealytic *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 adjuster 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. (2009), 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.

Kawasaki et al. (2006) described the main advantages of using microorganisms in the geotechnical engineering field as follows.

1. Biological cement precipitation is slower than chemical reactions alone. This delay effect, in particular, may enable the technological control of the reaction time.
2. In situ microorganisms are an unused resource in the fields of engineering and rock mechanics. Their use would stimulate the development of novel technologies to lower costs and environmental damage.

Meanwhile, 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 kind 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.

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In nature, various minerals, such as calcium carbonate, calcium phosphate, calcium oxalate, silicate, and iron oxide, are precipitated by living organisms (Mann, 1988, 1993). These biominerals are promising as engineering materials because they have adequate strength and low environmental impact. In this study, we carried out a fundamental examination on new rock grout materials comprised of calcium phosphate compounds (CPCs) (Figure 1). CPCs exist as phosphate rocks (mainly fluoroapatite) in the natural environment and as an important inorganic substance (mainly hydroxyapatite, HA) in living organisms (Dorozhkin and Epple, 2002). 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 (Table 1). Research and development of materials comprised of CPCs are currently in progress, especially in the fields of medicine and dentistry (e.g., see Martin and Brown, 1995; Bohner et al., 2006; Ginebra et al., 2006).

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 rock grout material that is precipitated under normal temperature and pressure, with easily handled materials through microbial activity. To the best of our knowledge, no existing rock 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 (Figure 2; Chow, 1991; Tung, 1998). Consequently, CPC hardens after injection into soil and rock because of the self-setting mechanism (Ginebra et al., 1997).
2. The solubility of CPCs depends on the pH of the surrounding environment (Figure 3; Tung, 1998). 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 marine 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 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 as well as measures to prevent 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 Figure 1). Subsequently, test pieces composed of Toyoura sand cemented by CPC were subjected to unconfined compressive strength (UCS) tests and observed by scanning electron microscopy (Step 2 in Figure 1). Our aim was to evaluate the feasibility of using the novel grout as a chemical grout and a microbiological grout by exploiting the self-setting property of CPC and the microbial pH adjustment activity in CPC precipitation, respectively.

Table 1
Properties of biologically relevant calcium orthophosphates (Dorozhkin and Epple, 2002).

Ca/P ratio	Compound	Abbreviation	Formula
0.5	Monocalcium phosphate monohydrate	MCPM	$Ca(H_2PO_4)_2 \cdot H_2O$
0.5	Monocalcium phosphate anhydrate	MCPA	$Ca(H_2PO_4)_2$
1.0	Dicalcium phosphate dihydrate	DCPD	$CaHPO_4 \cdot 2H_2O$
1.0	Dicalcium phosphate anhydrate	DCPA	$CaHPO_4$
1.33	Octacalcium phosphate	OCP	$Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$
1.5	A-tricalcium phosphate	α-TCP	α-$Ca_3(PO_4)_2$
1.5	B-tricalcium phosphate	β-TCP	β-$Ca_3(PO_4)_2$
1.2–2.2	Amorphous calcium phosphate	ACP	$Ca_x(PO_4)_y \cdot nH_2O$
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. Materials and methods

2.1. In vitro precipitation test of CPC

In this study, reagents with relatively high solubility were chosen for convenient handling during practical application. Monoammonium phosphate (MAP, pH 4.2 (The Merck Index, 2001)) and diammonium phosphate (DAP, pH 8.0 (The Merck Index, 2001)) were used as the components of the phosphate stock solution—a kind of agricultural fertilizer that can be prepared easily. The pH of the phosphate stock solution can be adjusted simply by changing the mixture ratio of MAP and DAP; hence, the components (phosphate ions and ammonium ions) of this material need not be varied to change the pH. To evaluate the effect of pH on the crystal precipitation of CPC, ammonium phosphate (AP) stock solutions with 11 different levels of pH were made by mixing MAP and DAP in proportions ranging from 10:0 to 0:10. For example, if 1 M MAP and 1 M DAP were used, the pH of the 11 resulting solutions ranged from 4.2 (10:0) to 8.4 (0:10). For the calcium stock solution, calcium nitrate (CN) or calcium acetate (CA) was used.

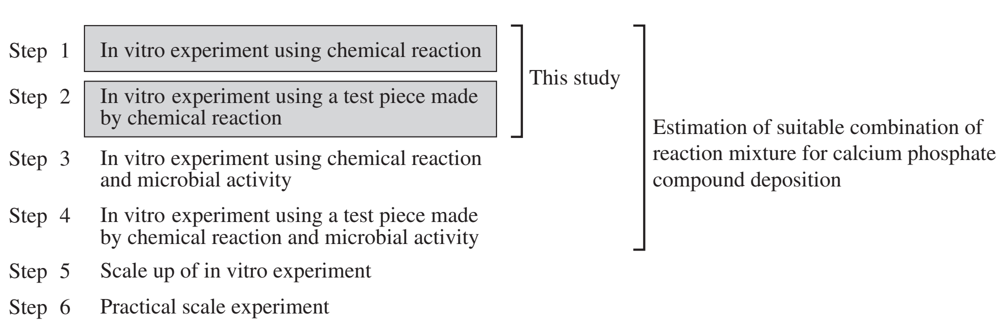

Fig. 1. Flowchart of the study. The steps carried out in this study are highlighted in gray.