

SOIL IMPROVEMENT USING CALCIUM PHOSPHATE COMPOUNDS AS A NOVEL SUSTAINABLE METHOD: A REVIEW

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ABSTRACT: Many new soil reinforcement techniques have recently emerged, the most popular of which are microbial-induced carbonate precipitation (MICP) and enzyme-induced carbonate precipitation (EICP). They are environmentally friendly and more sustainable than conventional methods for soil stabilization, however during carbonate (e.g., calcite) precipitation, ammonia (NH₃) and ammonium (NH₄⁺) emissions are released into air and groundwater, which are hazardous. There are techniques for removing NH₄⁺ from the soil, however, the ammonia problem remains to be addressed. By using calcium phosphate compounds (CPCs), ammonium emissions can be eliminated by more than 90%. The precipitation of calcium phosphate occurs when the calcium and phosphorus sources interact at increasing pH of the medium. Deposition type of CPCs depends on pH of environment and Ca/P ratio of solution. The most common precipitation methods are: 1) mixing calcium and phosphorus sources directly; and 2) mixing urea and acid urease or acidic bacteria with Ca and P sources. Deposition takes place in between sand particles enhancing their contact and, therefore, strengthens the soil. Given the relatively low popularity and lack of research on CPCs for soil improvement, this review discusses soil improvement methods using CPCs, their prospects, and their limitations. In addition, it will also show differences in products when using different methods of obtaining CPCs and merits of using CPCs.

Keywords: Soil improvement; Calcium Phosphate Compounds (CPCs); Morphology; pH dependency; Ground improvement.

1. INTRODUCTION

Soil is a porous natural material that needs to be compacted or strengthened before it can be used for engineering purposes. This is a critical, non-renewable material that needs to be efficiently used. Therefore, it is vital to understand how to use it in environmental and sustainable conditions [1], [2]. According to [3], soils for engineering applications can be divided into: Gravels, Sands, Silts and Clays and Highly Organic Soils. For each type of soil, there are appropriate techniques to strengthen it. In general, soil stabilization methods can be divided into (I) Chemical methods, (II) Biological methods and (III) Mechanical methods.

Chemical stabilization involves adding additives to the soil to obtain the desired physical and mechanical characteristics. Chemical methods of soil stabilization consist of on-site work and mixing the soil with cement, asphalt, silicates, bentonite, ash, polymers, fly ash, silica fume, blast furnace slag, gypsum, calcium-based chemicals and lime, acids, salts, petroleum emulsions, resins and lignosulfonates. Biological methods are a mixture of environmental practices and engineering techniques and include the use of bio-organisms and/or their byproducts as a structural component. Mechanical stabilization involves methods and techniques by which air voids can be removed from the ground with a nominal

change in water content to strengthen it. Mechanical methods are the oldest, most common techniques and include synthetic reinforcement application. Displacement and replacement, soil nailing, stage constructions, stone columns method and preloading, reinforcing bars, fibers, grids, strips are the most used techniques [4-6].

Due to the rapid growth of the world's population, there is a rising demand for reinforced and prepared soils for engineering purposes. Therefore, there is a growing interest in finding alternative, environmentally friendly and harmless methods of soil strengthening or improving the existing ones. Sustainable engineering practices rank first worldwide in encouraging and incentivizing use. The construction industry alone accounts for 23% of the global carbon dioxide (CO₂) emissions, with Portland cement production responsible for 6% of those emissions. This motivates for the need to discover new environmentally friendly methods and these techniques must be implemented in the field of engineering, including geotechnical engineering [7].

A relatively new method that is rapidly gaining popularity is biocementation. Biocementation is a geotechnical process that utilizes microorganisms to bind the soil particles, which significantly increases the strength of soil [8]. Mainly, this process used in two major biochemical methods: microbial-induced carbonate precipitation (MICP) and enzyme-induced

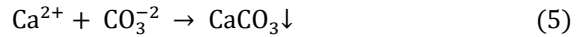
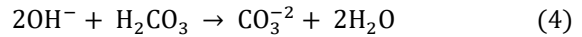
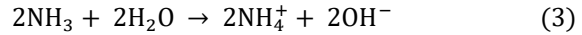
carbonate precipitation (EICP).

MICP is a process where the bacterium produces a urease enzyme that reacts with urea ($\text{CO}(\text{NH}_2)_2$), converting it into ammonium (NH_4^+) and carbonate ions (CO_3^{2-}) Eq. (1) - (4). This process raises the pH of the environment, resulting in higher emissions of ammonia (NH_3) into the atmosphere and ammonium into the water. Calcium ions (Ca^{+2}), in turn, react with CO_3^{2-} to produce calcium carbonate (CaCO_3) at the nucleation sites provided by the bacteria cells Eq. (5). Precipitation of calcium carbonate can be achieved by urease produced bacteria (MICP) or by using a urease enzyme directly (EICP). With urease source being the different factor between the two methods, the reaction pathways are similar (Fig. 1) [6, 9]. Figure 1 demonstrates that after the synthesis of urease by the bacterium, MICP and EICP methods follow the same procedure.

Although MICP and EICP are significantly more environmentally friendly than conventional soil-reinforcement methods, they have their limitations.

(I) a byproduct produced during urea hydrolysis

is ammonia (which release to atmosphere) and ammonium (which pollute ground water) and hydroxide ions. This occurs according to the following equations Eq. (1) - (5):



(II) relatively fragile bonding of soil particles due to non-uniform deposition of CaCO_3

(III) the reaction pathway is slow and more complex compared to chemical agents

(IV) the use of commercially available calcium reagents is less cost effective when compared to convention cement [8, 10].

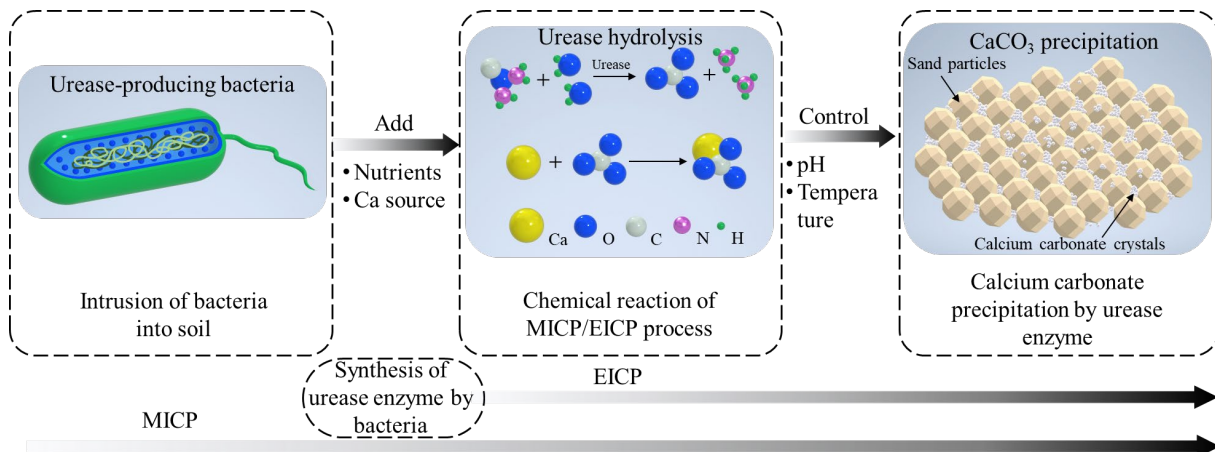


Fig.1 Schematic representation of MICP and EICP process

2. RESEARCH SIGNIFICANCE

Technology of deposition of calcium-phosphate compounds is a promising methodology in the development of ecological methods of soil stabilization. This is a novel and viable method that remains to be explored and implemented in the geotechnical sector. Application of CPCs for soil stabilization allows to solve the problem of ammonium pollution and improves existing biocementation methods towards more environmentally friendly level. CPCs demonstrate relatively high strength compared to MICP and EICP methods, as well as advantages over them in environmental friendliness, non-toxicity, the possibility of recycling and the self-setting mechanism that strengthens itself over time. Therefore, this method needs to be further investigated and developed for future prospective use.

3. LIMITATION OF CONVENTIONAL METHODS OF BIOCEMENTATION

Ammonia (NH_3) is a colorless gas with a density similar to air, 0.73 kg/m^3 . During MICP/EICP, large amounts of NH_3 and NH_4^+ are released into atmosphere and water, respectively. In small quantities, these substances are not harmful to humans or animals, but large quantities of NH_3 can cause severe illness and even death in animals [11]. This has resulted in the legislation in Japan where the maximum concentration of ammonium in industrial wastewater $<100 \text{ mg/L}$ [12]. As a byproduct of MICP and EICP, 10.500 mg/L and 11.200 mg/L of ammonia and ammonium pollute environment, respectively [13]. These emissions are 100 times higher than the limits, which has led to only a handful of studies conducted in large-scale applications [14]. During conventional MICP/EICP, the pH of the medium

increases to 8.8-9.0, resulting in the precipitation of calcium carbonate [15]. Figure 2 shows that up to pH 7.3, the formed nitrogen is in its NH_4^+ form, and after pH 7.5 it is almost completely converted into gaseous form, releasing a large amount of gas into the atmosphere, which accordingly prevent these methods from being applied in the field. During urease hydrolysis, 1 mol of urea produces 1 mol of carbon dioxide (CO_2) and 2 mol of ammonia (NH_3). One part of NH_3 turns into NH_4^+ in the solution, the part goes into gaseous phase and pollutes the air, and the other part remains in the solution as $\text{NH}_3 \cdot \text{H}_2\text{O}$. Therefore, most of the NH_3 gas produced during the biocementation process is uncontrollable and gets released into the environment, resulting in pollution [11].

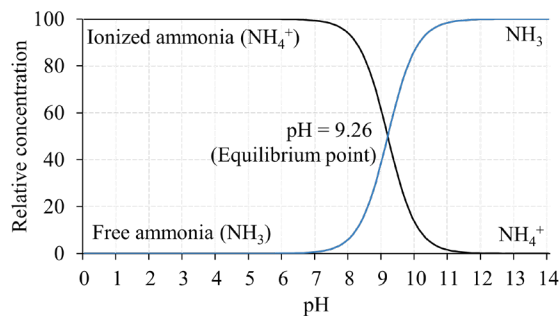


Fig.2 Dependence of ammonium and ammonia relative concentration and pH (modified from [16])

Scientists from all over the world are trying to solve the problem of NH_3 gas and NH_4^+ produced during the MICP/EICP process. If their formation is inevitable, it is necessary to control the course of the reactions. Among the effective techniques are rinsing technique (with NH_4^+ removals exceeding 99.8%) [17], electro-biocementation (allows to minimize emission of NH_4^+ into the soil) [18], the addition of zeolite (up to 75%) [19], absorbance of released NH_3 by sulphuric acid [10, 20], precipitation NH_4^+ as struvite (up to 97.79%) [11, 21].

4. CALCIUM PHOSPHATE COMPAUNDS

A potential, alternative method to reduce emissions of toxic NH_3 gas to the environment is biogrouting by calcium phosphate compounds (CPCs) precipitation. The deposition of CPCs occurs when the calcium and phosphorus sources interact at increasing pH of the medium. First type of biogrouting occurs due to CPCs precipitation using phosphate and calcium source solutions [22]. Second – due to CPCs precipitation obtained via reaction between bacteria, urea, calcium and phosphate source [23, 24]. In the first type, the reactions take place through an acid-base reaction, in the second - through the hydrolysis of urea. In both reactions, an increase in the pH of the medium is necessary for the

precipitation of calcium phosphates. CPCs has an adequate physical strength (unconfined compressive strength (UCS) 0.1-2.0 MPa) [22, 23, 25-32], and are promising geotechnical material.

Calcium phosphates are currently widely used for dental applications [1, 33, 34], bone tissue engineering [35], coating of implants, drug delivery and encapsulation [36], bioceramics [37-40] and strengthen the soil [22, 26-32, 41, 42]. The benefits of using this family of compounds for strengthening soils are the following:

- CPCs are environmentally friendly and non-toxic materials. The basic mineral hydroxyapatite with a Ca/P molar ratio of 1.67 is the most documented and investigated calcium phosphate and is the mineral that makes up bones and teeth [33].
- CPCs become stronger over time through a self-setting mechanism. Amorphous or gel-like calcium phosphate turns into a stable form, HA (Fig.3).

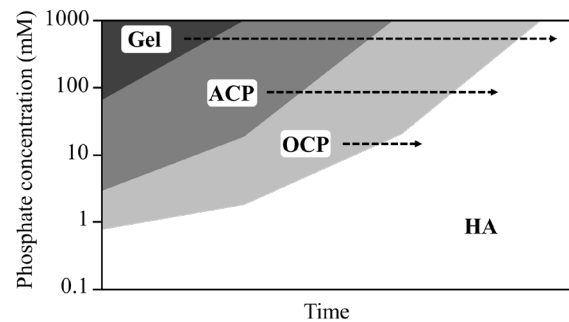


Fig.3 The dependence of calcium phosphate presence [22]

- The solubility of CPCs depends directly on the pH of the medium, so by controlling the pH solution you can control the minerals that will form (Table 1, Fig.4).

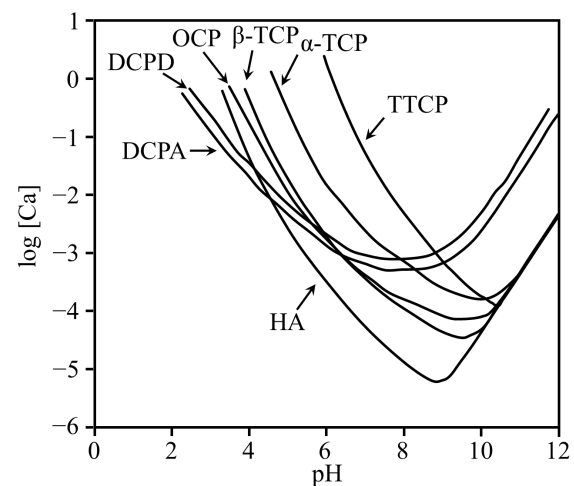


Fig.4 Solubility of each calcium phosphate compound as a function of pH [22]

Table 1 List of calcium phosphate compounds [30]

Ca/P ratio	Compound	Abbreviation	Formula
0.5	Monocalcium phosphate monohydrate	MCPM (MCP)	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$
0.5	Monocalcium phosphate anhydrate	MCPA (MCP)	$\text{Ca}(\text{H}_2\text{PO}_4)_2$
1.0	Dicalcium phosphate dihydrate	DCPD (DCP)	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
1.0	Dicalcium phosphate anhydrate	DCPA (DCP)	CaHPO_4
1.33	Octacalcium phosphate	OCP	$\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$
1.5	α -tricalcium phosphate	α -TCP	$\alpha\text{-Ca}_3(\text{PO}_4)_2$
1.5	β -tricalcium phosphate	β -TCP	$\beta\text{-Ca}_3(\text{PO}_4)_2$
1.2-2.2	Amorphous calcium phosphate	ACP	$\text{Ca}_x(\text{PO}_4)_y \cdot n\text{H}_2\text{O}$
1.5-1.67	Calcium-deficient hydroxyapatite	CDHA	$\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x} \quad (0 < x < 1)$
1.67	Hydroxyapatite	HA	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
2.0	Tetracalcium phosphate	TTCP	$\text{Ca}_4(\text{PO}_4)_2\text{O}$

- CPCs are recyclable. CPCs, that remain in the soil after applying various precipitation techniques can be removed and used as agricultural fertilizer [22, 23].

Along with its advantages, CPCs also have its disadvantages. They have low strength, and it is challenging to control the reaction and precipitation. Compared to UCS soil reinforced with CPCs and MICP/EICP, the strength of the soil is several times lower (0.1-2.0 MPa and 0.31-14.0 MPa respectfully) [6]. Due to the relatively low precipitation of CPCs ($\sim 28 \text{ kg/m}^3$), more calcium-phosphate resources are required to achieve a measurable strength in soils ($\sim 60 \text{ kg/m}^3$), resulting in a more expensive method [23].

Some researchers have used pure chemicals [22, 26-31]; and urease hydrolysis [12, 23, 25, 32, 41, 42] to improve soil with CPCs. The reaction of formation of CPCs during urease hydrolysis takes place at from weakly acidic to neutral pH, causing formation of almost all ammonium in ionic form, rather than in the most dangerous gaseous form. However, methods should be used to control and evacuate ammonium ions in the soil after treatment.

5. WAYS TO INCREASE STRENGTH OF CPCs

CPCs are weaker in strength than conventional methods for soil improving, which in turn limits their use for soil enhancement. Solving this problem will increase the capabilities and variability of CPCs implementation.

The following methods can be used to increase soil strength by applying CPCs:

- ammonia and ammonium can be turned into struvite, which not only solves the problem of contamination of the environment after the reaction of CPCs deposition, but also increases the strength of the soil [11, 43]. Using this practice together with the CPCs solves two challenges at once: low strength of soil and ammonium pollution.

- the most common method of strengthening building materials is the use of reinforcement. There are a wide variety of investigated fibrous materials - fibers. Both synthetic, such as glass fiber, plastic fiber, metal fiber, and natural fiber, such as plant fiber, fiber from animal components and mineral fiber, are used [4]. In CPCs, ceramic nanofibers are widely used for reinforcement [44].

- adding powders, such as tricalcium phosphate; magnesium phosphate; calcium carbonate and magnesium carbonate, and natural calcium and phosphorus-containing powders [28, 29, 31].

- in the case of microbial/enzymatic CPCs precipitation, pure chemical reagents can be used to improve the physical characteristics of the compounds. The other way to improve soil properties is to use bacteria with high urease activity or pure urease with calcium and phosphate chemicals. Application of urease or urease-producing bacteria together with CPCs precipitation method allows to obtain both CPCs and calcite in the precipitate, which increases the strength. UCS of soil can be increased by modifying the way the chemicals are applied to the soil, such as injection frequency or volume.

6. CPCs PRECIPITATION MECHANISM

The formation of CPCs depends on various factors, most important among which are the pH of the medium, the Ca/P ionic ratio and solubility. These parameters are highly correlated with the pH of the solution [45].

The reactions leading to the formation of CPCs could be divided into two types, the acid-base reaction, and the hydrolysis reaction. Only one calcium-phosphate source compound is involved in the hydrolysis reaction, which interacts with the liquid phase and transforms into the hydrate phase. On the other hand, during the acid-base reaction, the acid base and other bases interact with several

calcium-phosphate source compounds, with the formation of the final end-product with neutral pH [35, 46]. The precipitation mechanism of CPCs is similar for both types of reactions. In the initial stage, the aqueous solution becomes saturated with calcium and phosphorus ions, followed by reaching thermodynamic equilibrium. Thermodynamic equilibrium is the state at which, at constant pH, the solution is completely saturated without any excess calcium and phosphorus ions, enabling precipitation of CPCs [13].

From eleven well-known CPCs with a molar ratio of Ca/P in the range from 0.5 to 2.0 (Table 1), there are only six compounds that can be precipitated from aqueous solutions at temperatures below 100°C: MCPM, DCPD, OCP, ACP, CDHA and HA. Other compounds required high temperature and can harden as a result of solid-phase reaction [13].

Table 2 Major properties of CPCs [13]

Compound	Solubility at 25°C, g/L	pH stability range in aquatic solutions at 25°C
MCPM	~18	0.0-2.0
MCPA	~17	a
DCPD	~0.088	2.0-6.0
DCPA	~0.048	a
OCP	~0.0081	5.5-7.0
α -TCP	~0.0025	b
β -TCP	~0.0005	b
ACP	c	5-12
CDHA	~0.0094	6.5-9.5
HA	~0.0003	9.5-12
TTCP	~0.0007	b

a-stable at temperature over 100°C; b-these CPCs are not able to be precipitated from aquatic solutions; c-cannot be measured accurately.

According to the final product of deposition, CPCs can be divided into two groups: apatitic and brushite CPCs. The desired end product can be predicted depending on the solubility of CaP precursor and the pH of setting reaction. The final products of apatitic CPCs are either CDHA or HA. Apatitic CPCs can be formed either by acid-base interactions or by hydrolysis reactions. Brushite CPCs are acidic, and reactions can also occur at pH < 2.5. Thus, this type of CPCs can only be formed due to the reactions of the acid base with DCPD as the final product. Apatitic CPCs are less soluble than brushite CPCs. Brushite has a short setting time, so it is more porous and non-strength. For this reason, most CPCs are apatite CPCs [35, 46].

Table 3 shows main acid-base reactions of deposition apatitic and brushite CPCs. Hydroxyapatite, the most stable and strongest mineral, precipitates over time, as a result of increasing pH and calcium concentration in the system (Table 3, Fig.3).

Table 3 Acid-base reactions of precipitation CPCs [47]

Compound	Reaction
ACP	$x\text{Ca}^{2+} + y\text{HPO}_4^{2-}/\text{PO}_4^{3-} + n\text{H}_2\text{O} \rightarrow \text{ACP} \downarrow$
DCPD	$\text{Ca}^{2+} + \text{HPO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{DCPD} \downarrow$
OCP	$8\text{Ca}^{2+} + 4\text{PO}_4^{3-} + 2\text{HPO}_4^{2-} + 5\text{H}_2\text{O} \rightarrow \text{OCP} \downarrow$
HA	$10\text{Ca}^{2+} + 6\text{PO}_4^{3-} + 2\text{OH}^- \rightarrow \text{HA} \downarrow$
	$\text{OCP/DCPD/ACP} + x\text{Ca}^{2+} + y\text{OH}^- \rightarrow \text{HA} \downarrow$

According to the triprotic equilibrium for orthophosphate-containing solutions, a change in pH leads to a change in the relative concentrations of the four main types of orthophosphoric acid, resulting in a change in the type of precipitated CPCs (Fig.5). Hence, the pH of the solution is crucial for the precipitation of calcium-phosphate compounds. Changing the pH in the deposition interval (Fig.4) allows to control the precipitated compounds and thus the characteristics of the CPCs.

As an alternative method to increase the pH of the solution, it is possible to use microbial cultures or urease with a high urease activity in the acidic range.

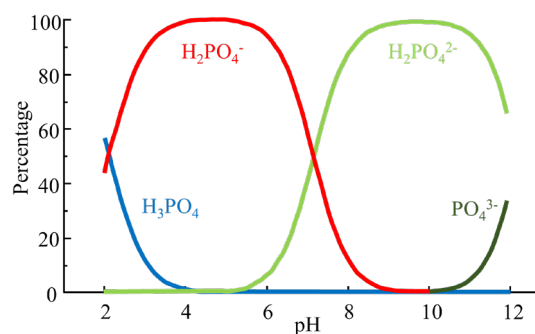
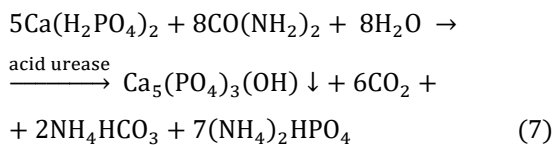
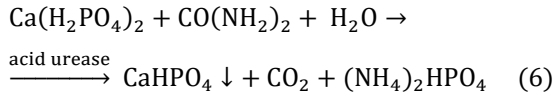


Fig.5 pH dependence of ion concentration in triprotic equilibrium for solutions of orthophosphoric acid (modified from [48])

CPCs can be formed due to acid tolerant urease-producing microorganisms or acid urease by the following DCPA and HA precipitation reaction Eq. (6) and Eq. (7) respectively [8].



The application of bacteria can control the pH of the environment, which will control the products that will eventually be formed. Moreover, it allows the deposition of calcite simultaneously with calcium phosphate. The precipitation of several minerals together can solve a low strength issue of the CPCs alone.

7. CONCLUSIONS

The application of CPCs for soil reinforcement is a novel, environmentally safe method in civil and geoenvironmental engineering. Implementation of these compounds can address the problem of toxic emissions in a real field application. Due to the size of the enzyme or chemicals, CPCs can be used for compact soils with a small gap between particles. Applying different fibers at different levels, from micro to nano levels, can significantly increase soil strength and facilitate the process of soil injection.

CPCs are highly dependent on the pH of the medium and the ratio of calcium and phosphorus in the solution. The precipitation process is hardly controllable, however eventually all CPCs are converted to hydroxyapatite due to a self-setting mechanism, making them promising methods in the long-term application range. By changing the ratio of chemicals or using natural sources of calcium or phosphorus, it is possible to make these methods more cost effective. Phosphorus is a limited resource that decreases every year [49], however, by using CPCs for soil stabilization, it is possible to reuse phosphorus from the soil, as CPCs are non-toxic and recyclable. Alternatively, it is possible to use acidic bacteria from food products along with modification of urease activity to enhance the performance. Since these bacteria are harmless to humans, it greatly accelerates the waiting period before application to the open field.

Therefore, implementation of CPCs for soil strengthening is a promising technology that has advantages over traditional methods of biocementation. The application of the experience of using MICP and EICP methods for the deposition of CPCs would allow to increase of their characteristics and improve the existing methodology. Nevertheless, these techniques still need further research and improvement in the future to be completely environmentally friendly.

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