A comparative investigation of using microbial- and CO₂-induced carbonate minerals in sustainable soil Improvement

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Research Article

Keywords: MICP, CO₂ capture, Carbonate mineral, Soil improvement

Posted Date: February 1st, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1207809/v1>

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Abstract

The structure and shape of carbonate crystals formed by microbial activity and carbon dioxide reaction were investigated in this work. The mineral carbonates treated sandy soil was subsequently determined using unconfined compression tests (UCS). *Sporosarcina pasteurii* bacteria were used to produce an aqueous solution of free carbonate ions (CO_3^{2-}) under laboratory circumstances called microbial-induced carbonate precipitation (MICP). In CO_2 -induced carbonate precipitation, carbon dioxide was added to a sodium hydroxide solution to form free carbonate ions (CO_3^{2-}) (CICP). Different carbonate mineral compositions were then provided by adding Fe^{2+} , Mg^{2+} , and Ca^{2+} ions to carbonate ions (CO_3^{2-}). In the MICP and CICP procedures, the results of scanning electron microscopy (SEM) and X-ray powder diffraction (XRD) revealed a distinct morphology of carbonate minerals. Vaterite (CaCO_3), siderite (FeCO_3), magnesium carbonate hydrate, or Nesquehonite ($\text{MgCO}_3 \cdot (\text{H}_2\text{O})_3$) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) were produced in MICP. Calcite (CaCO_3), siderite (FeCO_3), magnesium carbonate hydrate or Nesquehonite ($\text{MgCO}_3 \cdot (\text{H}_2\text{O})_3$), and high-Mg calcite ($\text{CaMg}(\text{CO}_3)_2$) were produced in CICP. The results of UCS showed that siderite and high-Mg calcite /dolomite had more efficiency in soil strength. The lowest value of strength was related to magnesium carbonate hydrate treated soils. Mineral-treated soils in CICP showed a slightly higher UCS strength than MICP, which could be attributable to greater crystal particle sizes and particle interlocking.

1. Introduction

Sustainable precipitation of carbonate minerals may provide green means of mitigating some geotechnical challenges associated with soils. Microbial-induced carbonate precipitation (MICP) and CO_2 -induced carbonate precipitation (CICP) can induce interparticle cementation and mineral precipitation in soil pore space to address geotechnical problems such as soil erosion and slope instability (Keykha et al. 2017, Keykha et al. 2018a, Romiani et al. 2021).

Biomineralization is the chemical modification of an environment that comes about within the precipitation of minerals by microbial activity which may be extracellular precipitation. The carbonate precipitation as a result of extracellular mineralization is a well-known phenomenon in all classes of living organisms. (Lowenstam and Weiner 1989). While precipitation of carbonate as an inorganic chemical reaction is difficult in natural environments, bacteria can cause mineral precipitation in microenvironments by (1) changing surrounding environmental conditions, and (2) acting as nucleation sites (Sánchez-Román et al. 2011). The negative surface charge of bacterial cells absorbs divalent cations (e.g. Ca^{2+} , Mg^{2+}) at neutral pH, making them suitable nucleation sites for calcite deposition. (Ferris et al. 1997; Stocks-Fischer et al. 1999). Microbial-induced carbonate precipitation (MICP) is a biogeochemical process that precipitates calcium carbonate as extracellular mineralization. MICP treatment is a CaCO_3 precipitation technology that biologically uses ureolytic bacteria to hydrolyze urea to carbonate by producing urease enzyme release. (Ivanov and Chu 2008). However, the CaCO_3 formation of bacteria is challenging in the soil environment as the mineralization is occurring by a living organism.

MICP can produce different polymorphs of CaCO_3 such as aragonite, calcite, and vaterite, as well as hydrated crystalline phases such as hexahydrocalcite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$), monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$), and amorphous calcium carbonate (Chen et al. 2009; Gebauer et al. 2010). The culture media can affect crystal morphology because different bacterial species precipitate different types and shapes of carbonate crystals from the same medium (Ferrer et al. 1988; Hammes and Verstraete 2002; Dhami et al. 2013). Depending on the polymorph of CaCO_3 crystals (i.e. calcite, vaterite, or aragonite), the strength of biocemented soil can be affected (Al-Thawadi 2013; Dhami et al. 2013). Less information is available concerning the usage of other carbonate minerals for soil improvement.

The precipitation of carbonate minerals by CO_2 transformation is considered a promising option for carbon capture and storage (CCS) since (i) CO_2 can be accumulated permanently and (ii) industrial disposals (i.e. cement and lime kiln dust, steel, and stainless-steel slags, etc.) can be recycled into carbonate materials by controlling polymorphs and properties of the mineral carbonates (Chang et al. 2017). CO_2 may be stored and converted to carbonate minerals for a long time such as CaCO_3 and MgCO_3 because they are stable forms of carbon (Smit et al. 2014). In addition, mineral carbonation also has unique advantages because allows the utilization of industrial wastes (with hazardous effects), and given this providing an appropriate method for disposal or recycling is a significant environmental issue. According to a recent study, MICP improves soil characteristics by precipitating carbonate minerals between soil particles in an environmentally friendly method. (Romiani et al. 2021). It entails capturing carbon dioxide (carbon sink) and producing carbonate minerals as a result (e.g. siderite, magnesite, and calcite). The carbonate minerals are environmentally safe and have the potential to physically and chemically bind soil particles. The developed MICP and their application in soil improvement is a promising result for new efforts because carbon dioxide is a contributing factor to the major global warming projected in future decades.

This research aims to evaluate the structure and morphology of carbonate crystals that form as a result of microbial activity and CO_2 reaction, as well as to compare the effects of minerals on soil treatment.

2. Materials And Methods

2.1. Microbial induced- ammonium free carbonate production

The *Sporsarcina pasteurii* (PTCC 1645) a urease-producing bacterium was used in this study. *S. pasteurii* was harvested using NH_4 -YE, a medium made up of 20.0 g yeast extract in 100 ml distilled water, 10.0 g $(\text{NH}_4)_2\text{SO}_4$ in 100 ml distilled water, and 0.13 mol/lit tris buffer (pH = 9.0). After that, the materials were autoclaved separately (121°C for 15 minutes), cooled, and then blended in an Erlenmeyer flask. The bacteria medium was cultured at a pH of 9.0, which is ideal for the growth of *S. pasteurii*. The bacteria were thereafter moved to the medium broth in an incubator (30°C) and shaken at 200 rpm under aerobic conditions for 2–3 days. The bacterium was extracted from an overnight culture by centrifugation

(Sartorius AG, sigma 3-18 K, Germany) at 8000 g for 10 min with an optical density of 1.6 at 600 nm (Labomed UVD 2950). During cultivation, cell concentration was obtained about 10^8 cells ml^{-1} by measuring the OD600 using a spectrophotometer (Thermo Electron Corporation, Madison, WI).

To prepare a free carbonate solution, 100 ml urea (1M) was added to 100 ml of the culture bacteria. The bacteria were exposed to the urea and produced carbonate ions (CO_3^{2-}) according to equation 1. To separate the carbonate-producing bacteria, after 2 days, the solution was centrifuged at 10000 g for 8 min. The remaining solution (supernatant) was collected with a pipette and passed through a Millipore HPLC Syringe Filter (0.25 μm). The concentration of carbonate ion in the cementation solution was measured by Thomas Combination Carbonate Ion-Selective Electrode (ISE)

Bacterial cells + $\text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O} \rightarrow \text{CO}_3^{2-} + 2\text{NH}_4^+$ (equation 1)

In the next step, natural zeolite (sodium-potassium form, Pars Chemical industry) was used to reduce the ammonium ions according to the method developed by Keykha et al. (2018 b). In this study, different masses of zeolite powder were added to carbonate solution and remained for 3 days. The solution then was passed through filter paper and the ammonium concentration was measured using an Orion ion-selective ammonia probe (model no. 9512HPBNWP).

2.2. CO_2 induced-carbonate production

To produce free carbonate ions (CO_3^{2-}) in this study, a 2.5 kg industrial cylinder of CO_2 gas with relative density and solubility in water of 1.5 and 2000 mg/l was used respectively. Sodium hydroxide (NaOH) with molar masses of 39.99 g/mol and a density of 2.13 g/cm³ (as powder) was also used.

Free carbonate ions (CO_3^{2-}) were produced through laboratory-scale carbon capture technology (Inoue et al. 2010). To prepare free carbonate ions (CO_3^{2-}), the CO_2 gas was injected into a solution of sodium hydroxide (2 molar) at a 5 ml/min rate for a period of 72 h. In this process, when CO_2 reacts with water, in the presence of sodium hydroxide (NaOH), it forms Na_2CO_3 according to equation 2. The concentration of carbonate ions was eventually measured by Thomas Combination Carbonate Ion-Selective Electrode (ISE) at the end of the process.

$\text{CO}_2 + \text{NaOH} + 2\text{H}_2\text{O} \rightarrow \text{NaHCO}_3 (\text{aq})$ (equation 2a)

$\text{NaHCO}_3 (\text{aq}) + \text{NaOH} (\text{aq}) \rightarrow \text{Na}_2\text{CO}_3$ (equation 2b)

$\text{Na}_2\text{CO}_3 \rightarrow 2\text{Na}^+ (\text{aq}) + \text{CO}_3^{2-} (\text{aq})$ (equation 2C)

2.3. Carbonate minerals production

A schematic diagram of the carbonate mineral precipitation techniques is shown in Figure 1. Ferrous sulfate (FeSO_4), magnesium sulfate (MgSO_4), and calcium chloride (CaCl_2) were used to extract the ion

components of Fe^{2+} , Mg^{2+} , and Ca^{2+} , respectively. The chemical characteristics of the materials utilized are listed in Table 1.

Table 1
Chemical Properties of used materials and various ratios of ingredients

Type of material	Molar mass (g/mole)	Density (g/cm ³)	Ingredient rations	Type of mineral deposition
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	2.84	$\text{Fe}^{2+} : \text{CO}_3^{2-}$	1:1 FeCO_3
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	246.48	2.66	$\text{Mg}^{2+} : \text{CO}_3^{2-}$	1:1 MgCO_3
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	147.02	2.15	$\text{Ca}^{2+} : \text{CO}_3^{2-}$	1:1 CaCO_3
$\text{MgSO}_4 / \text{CaCl}_2$	246.4/147.02	2.66/2.15	$\text{Mg}^{2+} / \text{Ca}^{2+} : \text{CO}_3^{2-}$	1:1 CaCO_3 & $\text{CaMg}(\text{CO}_3)_2$

In this study, the carbonate minerals were precipitated by adding Fe^{2+} , Mg^{2+} , and Ca^{2+} ions to free carbonate ions (CO_3^{2-}) produced by microbial-induced carbonate precipitation (MICP) and CO_2 -induced carbonate precipitation (CICP). The FeCO_3 (siderite) was precipitated by adding ferrous sulfate solution (1molar) to free carbonate ions (CO_3^{2-}) produced by microbial induced carbonate or CO_2 induced carbonate precipitation (eq3a). The MgCO_3 (magnesite) was precipitated by adding magnesium sulfate solution (1molar) to free carbonate ions (CO_3^{2-}) (eq 3b). The CaCO_3 (calcite) was precipitated by adding calcium chloride solution (1molar) to free carbonate ions (CO_3^{2-}) (eq 3c). In addition, a blend of magnesium sulfate and calcium chloride (1molar) with rate 1:1 was added to free carbonate ions (CO_3^{2-}) to precipitate CaCO_3 (calcite) and $\text{CaMg}(\text{CO}_3)_2$ (dolomite) together (eq 3d). The carbonate solutions were centrifuged at 8000 g for 10 min and were eventually filtered by filter paper to obtain a condensed carbonate minerals solution with moisture contents in the range of 30-40%. The produced carbonate minerals from two different methods (Microbial-induced mineral carbonates and CO_2 -induced mineral carbonate) were used to test for SEM analysis and soil engineering properties in the next steps.

2.4. Scanning electron microscope (SEM)

The size, shape, and crystalline formation of the mineral crystals were examined using scanning electron microscopy (SEM) on the various mineral products from MICP and CACP. The specimens were gold-coated to make them conductive. For these trials, the accelerating voltages were chosen between 10 and 15 kV.

2.5. Green soil improvement using carbonate minerals

In this experiment, clean silica Firoozkuh sand was employed. The sand grain size distribution curve is shown in Figure 2. The sand had a specific gravity of 2.65, a uniformity coefficient of 2.75, and maximum and minimum void ratios of 0.91 and 0.57, respectively.

The soil specimens were prepared by mixing condensed carbonate minerals (i.e., siderite, magnesite, calcite, and calcite/dolomite). To obtain condensed carbonate minerals, the solutions were centrifuged at 8000 g for 10 min and were eventually filtered by a filter paper (Keykha et al. 2021). The carbonate minerals (with a water content of about 100%) were used as soil stabilizing agents in the unconfined compression tests.

2.5.1 Unconfined compressive strength test

The unconfined compression test was used for obtaining the approximate strength of the soil specimens. To perform the unconfined compression tests, the pre-weighed amount of sand was mixed with condensed carbonate minerals and placed in the two-piece split mold by slightly tamping to obtain a homogenous specimen of 50mm diameter and 100 mm length by dry density equal to about 19.2 kN/m^3 . Before the unconfined compressive strength tests, the specimens were allowed to cure at room temperature for 7 days. Table 2 shows a summary of the testing program and specifications of specimens.

Table 2
Testing program and specimens specifications

Sample Code	Mineral Type	Carbonate mineral (%)	γ_d (kN/m ³)	w (%)
Mg-MICP	MgCO ₃ by MICP	11.7	19.09	11.5
Mg-CICP	MgCO ₃ by CICP	13.2	19.35	9.7
Ca- MICP	CaCO ₃ by MICP	12.5	19.23	8.2
Ca- CICP	CaCO ₃ by CICP	12.7	19.26	9.3
Fe- MICP	FeCO ₃ by MICP	12	19.14	9.2
Fe- CICP	FeCO ₃ by CICP	12.3	19.19	10.1
(Ca-Mg)- MICP	(Ca-Mg)CO ₃ by MICP	13.7	19.43	9.5
(Ca-Mg)- CICP	(Ca-Mg)CO ₃ by CICP	13.4	19.38	10.6

The unconfined compression tests were repeated three times for each type of mineral and production method. The accuracy analysis was performed for parallel tests. The unconfined compressive strength (UCS) was taken as the peak stress with the corresponding axial strain at failure in the stress-strain curve (ASTM D2166/D2166M-16, 2016).

The carbonate mineral percentage of the samples was determined by using an acid washing technique (Keykha et al. 2018a). The soil samples were soaked into an acid solution (HCl 5 M). The dissolved carbonates and acid wash solution were filtered through a filter paper several times, allowing the dissolved salts to be rinsed from the soil while the soil was retained. Before and after the acid washing technique, the oven-dried mass of the soil samples across the specimen was measured. The mass of

carbonate minerals was calculated as the difference between the two observed masses. Table 2 shows the results that were achieved.

3. Results And Discussion

3.1. Induced carbonate production (CO_3^{2-})

In this study, the free carbonate ions (CO_3^{2-}) produced by microbial-induced carbonate (MICP) and CO_2 -induced carbonate (CICP) were compared in Figure 3. As it can be seen from the figure, a value of 42.1 and 34.8 g/lit were obtained for CICP and MICP methods, respectively.

The effect of Zeolite treatment on ammonium concentration for MICP to generate an ammonium-free carbonate solution is shown in Figure 4. The ammonium content of the solution was initially around 1.39g/lit, as seen in the figure. After 15 percent Zeolite treatment, the ammonium concentration dropped to an average of 3.4×10^{-5} g/lit. The concentration meets the requirement specified by some drinking-water standards (e.g. lower than 5×10^{-4} g/lit, Australian Drinking Water Guidelines and Guidelines for Drinking-water Quality Management for New Zealand, 2016).

3.2 Carbonate mineral production

Carbonate minerals precipitated by MICP and CICP techniques are shown in Figure 5. The results demonstrate that the carbonate minerals precipitated by CICP had higher values than those precipitated by MICP. The most carbonate minerals content were FeCO_3 (55g/lit) and Ca-Mg (CO_3) (58g/lit) precipitated by the CICP. The precipitation of CaCO_3 and Ca-Mg (CO_3) in MICP were identical (25 g/lit). In MICP, the highest level of carbonate precipitation was found in FeCO_3 (40g/lit), whereas the lowest level was found in MgCO_3 (8g/lit). As can be seen from the results in Figure 5, MICP deposited fewer carbonate minerals than CICP. It is generally accepted that this microbial activity can be influenced by several physicochemical and biological parameters, and it is correlated to both metabolic activities and cell surface structures (Zhong et al. 2016; Bazylnski and Moskowitz 2018). Multiple studies revealed that fresh bacterial cells are an essential step to keep the fast rate of precipitation, as desirable in certain applications (Murugan et al. 2021). CICP is a method based on the fixation of CO_2 in the form of inorganic carbonates, also known as 'mineral carbonation'. Since carbonate is the lowest energy state of carbon, these carbonation reactions are exothermic and the formation of carbonates is favored at low temperature and low pressure (Lead 2005).

3.4 Carbonate mineral characterization

Figure 6 illustrates the crystal morphology of CaCO_3 which was produced by MICP and CICP methods. As it can be seen, the CaCO_3 crystals have been grown spherical with diameters of 2-10 μm in MICP (Fig. 6a), while crystals were in rhombohedral shape and smooth with diameters of 2-6 μm in CICP (Fig. 6b). Figure 7 shows EDS and XRD analysis of CaCO_3 deposition. The EDS layered image presents the distribution of

C, O, and Ca elements in the test area. The result of XRD justified vaterite minerals (100%) (Fig. 7a) and calcite (100%) (Fig. 7b) in MICP and CICIP, respectively. In CICIP, deposition and morphology of CaCO_3 are dependent on additives such as CO_2 and Ca^{2+} which are precipitated in three anhydrous polymorphic modifications (calcite, aragonite, and vaterite) and mostly is calcite (Kralj et al. 2004). MICP is largely dependent on metabolic processes by ureolytic bacteria that influence crystal growth (Rahman and Oomori 2009; Marvasi et al. 2010; Wei et al. 2015; Bielak et al. 2021). It has also been reported that the amino acid (Glu (red) and Asp (blue)) in the urease enzyme favored the formation of vaterite (Sondi and Salopek-Sondi 2005).

Figure 8 shows the crystal morphology of FeCO_3 which was produced by MICP and CICIP methods. There was a similar crystal shape (spherical) for both of them. The particle size of FeCO_3 in MICP was with diameters of 0.5-3 μm while the particle size was bigger (2-6 μm) in CICIP. Figure 9 shows EDS and XRD analysis of FeCO_3 samples. The EDS layered image presents the distribution of C, O, Mg, and Fe elements in the test area. The result of XRD justified siderite minerals (100%) for MICP and CICIP. Less information is available concerning the mineralization or morphogenesis of iron carbonates (siderite). This is probably because natural siderite is often associated with other coexisting elements (e.g., Mn, Mg, and Ca), and contains a small amount of hematite (Fe_2O_3) due to partial oxidation in natural air (French 1971; Isambert et al. 2003). The biological aspects of iron biomineralization have been investigated by studying iron-bearing biominerals, owing to their significance in identifying microbe-sediment-water interactions, as well as mineral and biogenic origins (Frankel and Bazylnski 2003; Dong et al. 2009).

Figure 10 shows the crystal morphology of calcium magnesium carbonate which is produced by a mixture of magnesium and calcium ions with free carbonate ions (CO_3^{2-}). As it can be seen from the figure, there was a botryoidal crystal shape of calcium magnesium carbonate in the MICP method (Fig. 10a) while a flower-like shape was observed in the CICIP method (Fig. 10b). There was the main difference between the shape and size of crystals in both methods. The calcium magnesium carbonate was precipitated with diameters of 5-16 μm and 2-5 μm in MICP and CICIP, respectively. Minerals deposited in a larger size in MICP than in CICIP, as can be seen plainly. The EDS layered image presents the distribution of C, O, Mg, and Ca elements in the test area. XRD analysis of samples showed Ca-Mg (CO_3) deposition while was as dolomite (40%) and calcite (60%) in MICP (Fig. 11a) and high-Mg calcite (61%) and magnesium carbonate hydrate (Nesquehonite) (39%) in CICIP (Fig. 11b), respectively.

Previous laboratory research revealed that aerobic bacteria may have a role in the creation of high-magnesium calcite or dolomite, in the microenvironment around the cell (Sánchez-Román et al. 2009; Sánchez-Román et al. 2011; Al Disi et al. 2017). The increase of Mg^{2+} concentration (and the $\text{Mg}^{2+}:\text{Ca}^{2+}$ ratio) can also cause precipitation of dolomite and magnesite (Balci et al. 2016; Al Disi et al. 2019). Bacteria can adsorb Mg^{2+} on their membranes during induce dolomite formation, while calcite precipitation is induced by preferential adsorption of Ca^{2+} . González-Muñoz et al. (2010) found that Mg probably plays a key role in the development of the morphologies of the precipitates since these morphologies had never been observed in the absence of Mg. CaCO_3 mineral that has precipitated from

seawater changes from calcite to aragonite was experimentally determined as a function of temperature and additives. Results indicate precipitation of high-Mg calcite and dolomite is largely dependent on Mg:Ca ratio over a relatively small temperature range in an aqueous solution (Morse et al. 1997). In conclusion, the morphology, type, and size of calcium magnesium carbonate minerals are influenced by the chemical and biochemical environment in CICP and MICP.

Figure 12 illustrates the crystal morphology of MgCO_3 which was produced by MICP and CICP methods. As it can be seen, the MgCO_3 crystals have been grown in the radial needle (Fig. 12 (a, c)) and radial blades shape (Fig. 12 (b, d)) by MICP and CICP, respectively. There was the main difference between the sizes of crystals in both methods. The thickness of radial needle crystals was diameters of 1-10 μm in MICP, while it was precipitated in a greater thickness of about 5-20 μm as radial blades in CICP. It was clearly shown that the potential of CICP to precipitate MgCO_3 is more than MICP. Figure 13 shows EDS and XRD analysis of MgCO_3 samples. The EDS layered image presents the distribution of C, O, and Mg elements in the test area. The result of XRD explained the mineralization of magnesium carbonate hydrate (Nesquehonite) for both methods (Fig. 13). The magnesium carbonate (as hydrate) can display four different morphologies during the reaction process such as needle, sheet, rose, and nest-like with different carbonation temperatures (Zhang et al. 2007; Chen et al. 2020). Gautier et al. (2014) have studied the growth process of hydromagnesite by calculating its growth kinetics in an aqueous solution from 25 to 75°C. A previous study showed a similar morphology and type of $\text{MgCO}_3 \cdot (\text{H}_2\text{O})_3$ (Nesquehonite) that precipitated MICP (Zhao and Zhao 2017) and CICP (Glasser et al. 2016).

The mean size distribution of minerals was measured by SEM photos. Figure 14 shows the average size of carbonate minerals produced by MICP and CICP methods. As can be seen from the results, the average size of crystals was larger in CICP. Although there was only a small difference in calcium magnesium carbonate precipitation in MICP compared to CICP. The largest crystals in CICP, however, were for magnesium carbonate hydrate (Nesquehonite). In this work, CICP demonstrated a great capacity for precipitating carbonate minerals with larger sizes. The minerals that develop during biomineralization are frequently characterized by low crystallinity, structural well-ordering, and a limited size range. (Frankel and Bazylinski 2003). Under the same environmental conditions, biologically induced mineralization is equal to inorganic mineralization, and the minerals are expected to contain crystal-chemical characteristics that are indistinguishable from minerals formed by inorganic chemical reactions. However, cell walls of bacterial surfaces including biofilms, dormant spores, and slim sheaths can act as important sites for the adsorption of ions for growth and nucleation minerals (Bäuerlein 2003).

A summary of the characterization of carbonate minerals produced by MICP and CICP techniques is shown in Table 3. In both procedures, all carbonate minerals were precipitated in various sizes, shapes, and types.

Table 3
Characterization of produced carbonate minerals by MICP and CICIP

Name	Method	Type of Mineral	Size (μm)	Crystal Shape
Calcium carbonate	MICP	Vaterite	2-10	Spherical
	CICIP	Calcite	2-6	Rhombohedral
Ferrous carbonate	MICP	Siderite	0.5-3	Spherical
	CICIP	Siderite	2-6	Spherical
Magnesium calcium carbonate	MICP	Dolomite	5-16	Botryoidal
	CICIP	High-Mg calcite	2-5	Flower-like
Magnesium carbonate	MICP	Nesquehonite	1-10	Radial needle
	CICIP	Nesquehonite	5-20	Radial blades

Less information is available concerning the usage of other carbonate minerals for soil improvement. The solubility of carbonate minerals decreases by more than two orders of magnitude on transformation from Ca- to Mg-rich (Farsang et al. 2021). Mg carbonates such as magnesite and dolomite are semi-soluble and hydrophilic (Wonyen et al. 2018). Long et al. (2014) showed that the increase of Mg ions in the Mg-containing calcite improves the mechanical properties of biogenic minerals. As well as, ferrous carbonate has low solubility in an aqueous solution (Sun et al. 2009). It seems that carbonate minerals with substitution elements such as Mg and Fe affect on strengthens behavior of crystals in the soil improvement. Depending on the polymorph of CaCO_3 crystals (i.e. calcite, vaterite, or aragonite), the strength of biocemented soil can be affected (Al-Thawadi 2013; Dhami et al. 2013). It appears that calcite crystals with rhombohedral shape and high-Mg calcite with flower-like shape in CICIP have the capability of interlocking due to their surface roughness.

3.5 Unconfined compressive strength

Figure 15 shows the results of the UCS tests carried out on carbonate minerals-treated soil. As can be seen from the figure, the treated specimens with condensed $\text{Ca-Mg}(\text{CO}_3)$ and FeCO_3 minerals, produced by the MICP method gained about 58.5 kPa and 63.0 kPa UCS strength respectively (Fig. 15). Moreover, MgCO_3 minerals, produced by the MICP method had the lowest strength of about 25 kPa. The treated specimens with CaCO_3 content gained higher compressive strength compared to the specimens with MgCO_3 content in this study. The treated specimens with the CICIP method gained higher compressive strength compared to the specimens treated with the MICP method. The minerals produced by the CICIP method have a 15 to 28 percent higher compressive strength than those produced by the MICP method, according to the data.

The results of UCS showed that siderite and calcium magnesium carbonate (i.e. High-Mg calcite and dolomite) had more efficiency in soil strength as it seems to be because of the stability of Fe and Mg carbonate crystals. The treated soils by siderite in CICIP had slightly more strength more than MICP which

may be due to the larger particle size of siderite crystals. While the higher strength of high-Mg calcite in CICIP is related to surface roughness and more interlocking of particles. The strength of calcite-treated soil in CICIP was slightly more than vaterite-treated soil in MICP as well as may be related to the surface roughness of particles. The UCS result of magnesium carbonate hydrate (Nesquehonite) treated soil was lower than other carbonate minerals in this study. However, Nesquehonite (because of blade structure) had higher efficiency in clay soil in the previous study (Romiani et al. 2021). Moreover, the effect of Nesquehonite by CICIP with more thickness was more than needle minerals in MICP in the UCS test.

4. Conclusion

Microbial-induced carbonate precipitation (MICP) and CO₂-induced carbonate precipitation (CICIP) methods were used to create free carbonate ions (CO₃²⁻). The various carbonate minerals were precipitated by adding Fe²⁺, Mg²⁺, and Ca²⁺ ions to carbonate ions (CO₃²⁻). The carbonate minerals precipitated by CICIP were more precipitated than those precipitated by MICP, according to the findings. Carbonate minerals with distinct morphology in form and size crystals precipitated by MICP and CICIP were observed using SEM and XRD. Vaterite (CaCO₃), siderite (FeCO₃), magnesium carbonate hydrate or Nesquehonite (MgCO₃ (H₂O)₃), and dolomite (CaMg(CO₃)₂) were produced in MICP. Calcite (CaCO₃), siderite (FeCO₃), magnesium carbonate hydrate or Nesquehonite (MgCO₃ (H₂O)₃), and high-Mg calcite (CaMg(CO₃)₂) were produced in CICIP. The findings of UCS tests demonstrated an increase in strength for treated sandy soils by siderite and high-Mg calcite /dolomite that was more than treated soils by calcite/vaterite and magnesium carbonate hydrate (or Nesquehonite). Mineral-treated soils in CICIP were marginally stronger than MICP, likely due to larger crystal particle sizes or particle interlocking.

Declarations

Acknowledgment

This work has been supported by the Centre for International Scientific Studies& Collaboration (CISSC), Ministry of Science Research and Technology.

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Figures

Figure 1

Schematic diagram of carbonate mineral production

Figure 2

Particle size distribution of Firoozkuh silica sand

Figure 3

Concentration of CO_3^{2-} for MICP and CICP

Figure 4

Concentration of ammonium per different zeolite percentage

Figure 5

Carbonate minerals precipitation by MICP and CICP methods

Figure 6

SEM morphologies of CaCO₃ mineral (a) spherical shape by MICP (b) rhombohedral shape by CICP

Figure 7

EDS and XRD of CaCO₃ minerals (a) Vaterite by MICP (b) Calcite by CICP

Figure 8

SEM morphologies of FeCO_3 mineral with spherical shape in (a) MICP and (b) CICP

Figure 9

EDS and XRD of FeCO_3 mineral (a) Siderite by MICP (b) Siderite by CICP

Figure 10

SEM morphologies of Ca-Mg (CO_3) mineral (a) botryoidal shape by MICP (b) flower-like shape by CACP

Figure 11

EDS and XRD of Ca-Mg (CO_3) minerals (a) Dolomite and Calcite by MICP (b) High-Mg calcite and magnesium carbonate hydrate by CACP

Figure 12

SEM morphologies of MgCO₃ minerals (a) radial (c) needle shape crystals by MICP and (b) radial (d) blade shape by CICP

Figure 13

EDS and XRD of MgCO_3 minerals (a) magnesium carbonate hydrate (Nesquehonite) by MICP (b) Nesquehonite by CICP

Figure 14

The average size of precipitated carbonate minerals by MICP and CIP methods

Figure 15

Unconfined compressive strength of treated specimens with different carbonate minerals