Proceedings of the XVIII ECSMGE 2024
GEOTECHNICAL ENGINEERING CHALLENGES
TO MEET CURRENT AND EMERGING NEEDS OF SOCIETY

ISBN 978-1-032-54816-6
DOI 10.1201/9781003431749-457

Use of CO_2-induced siderite and dolomite with nanoclay for soil improvement

Utilisation de sidérite et dolomite induites par l' injection de CO_2 avec de la nanoargile pour l'amélioration de sols

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ABSTRACT: We studied the precipitation of carbonate minerals used as cements for ground improvement. The carbonate minerals were prepared by combining divalent ions (Mg^{2+}, Ca^{2+}, and Fe^{2+}) with carbonate ions (CO_3^{2-}) induced by microbial activity. Scanning electron microscopy (SEM) and X-Ray Diffraction (XRD) analyses observed the shapes and sizes of the minerals and attested the formation of dolomite ($CaMg(CO_3)_2$) and siderite ($FeCO_3$). Consolidated drained triaxial tests (CD) were performed on treated specimens of silica sand with the CO_2-induced siderite and dolomite cements with and without the addition of nanoclay. Specimens treated with siderite had higher strengths than dolomite-treated specimens. The addition of nanoclay further increased the shear strength of the specimens and reduced their brittleness. Moreover, it was found that the shearing resistance of fully saturated specimens was not considerably reduced compared to that of dry specimens, as it only decreased by 5–15% compared to that of dry specimens.

RÉSUMÉ: Nous étudions la précipitation de carbonates que nous utilisons comme ciments pour l'amélioration de sols. Les minéraux carbonatés ont été préparés en combinant des ions divalents (Mg^{2+}, Ca^{2+}, et Fe^{2+}) avec des ions carbonate (CO_3^{2-}) formés à partir de l'activité métabolique microbienne. La forme et la taille des minéraux ont été observées par analyses microscopiques (microscope électronique à balayage). L' analyse minéralogique des minéraux (par diffraction des rayons X) a confirmé la formation de dolomite ($CaMg(CO_3)_2$) et de sidérite ($FeCO_3$). Ces minéraux ont ensuite été utilisés pour l'amélioration des propriétés d'un sol granulaire. Des essais triaxiaux consolidés drainés (CD) ont été effectués sur des échantillons de sable siliceux traités par la sidérite et dolomite ainsi produites, avec ou sans nanoargile. Les échantillons traités à la sidérite avaient une résistance au cisaillement plus élevée que ceux traités à la dolomite. L'ajout de nanoargile a augmenté la résistance des échantillons au cisaillement ainsi que leur ductilité. De plus, la résistance des échantillons saturés n'était pas considérablement inférieure à celle des échantillons secs, n'ayant diminué que de 5 à 15% par rapport à celle des échantillons secs.

Keywords: MICP; siderite; dolomite; soil improvement.

1 INTRODUCTION

Sustainable precipitation of carbonate minerals has the potential to offer environmentally friendly ways of improving soils of poor engineering characteristics preventing soil erosion, slope instability, or low bearing capacity. Microbially-induced carbonate precipitation (MICP) has emerged as one such potentially more sustainable process, as it uses natural mechanisms to induce mineral precipitation in the soil pore space leading to soil cementation (Keykha et al., 2017, 2019; Wang et al. 2021, Romiani et al. 2023).

The precipitation of minerals by microbial activity, which may be extracellular precipitation, is known as biologically induced mineralization. In various types of living organisms, the extracellular mineralization-related carbonate precipitation is a well-known phenomenon (Lowenstam, 1989). By altering the surrounding environmental conditions and acting as nucleation sites, bacteria can promote mineral precipitation in microenvironments in some challenging natural conditions in terms of pH and temperature (Sánchez-Román et al. 2011).

MICP works have mostly studied $CaCO_3$ precipitation biotechnology using ureolytic bacteria to hydrolyse urea to carbonate by producing urease enzyme release as shown in equations 1-2 (Ivanov & Chu, 2008; Tang et al. 2020):

$$CO(NH_2)_2 + 2H_2O \xrightarrow{urease\ enzyme} CO_3^{2-} + 2NH_4^+ \quad (1)$$

$$CaCl_{2\,(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CaCO_3\,(s) \quad (2)$$

MICP can produce different polymorphs of $CaCO_3$ such as aragonite, calcite, and vaterite, as well as $CaCO_3$ monohydrate, $CaCO_3$ hexahydrate, and amorphous $CaCO_3$ (Mortensen et al. 2011).

This study aims to evaluate the use of various types of precipitated carbonate minerals other than only $CaCO_3$ to improve mechanical properties of soils. The minerals were obtained using carbonate ions (CO_3^{2-}) produced by the metabolic action of microbes as an *ex situ* process, to overcome complications of bacteria activity and survival in different soil environments. The carbonate minerals thus produced were then combined with nanoclay additive, to further enhance the mechanical properties of the treated soil.

2 MATERIAL AND METHODS

2.1 Bacteria type strain and culture media

The present study used urease-producing bacteria *Sporosarcina pasteurii* (PTCC 1645), grown in NH_4-YE, a medium made up of 800 mL of Tris-buffer 0.13 mol/L (pH = 9.0), 20.0 g of yeast extract, 10.0 g of $(NH_4)_2SO_4$, and 100 ml of distilled water. Before autoclaving, the pH of the growth medium solution was measured to be adjusted in 9.0. After that, the components were individually autoclaved (at 121 °C for 15 min) before being cooled and combined in an Erlenmeyer flask. Bacteria were cultivated at pH=9.0, which was the optimal pH for *S. pasteurii* growth. The bacteria were transferred to the medium broth in an incubator (30 °C) and shaken aerobically for 3 days at 200 rpm. A previously established optical density of 1.6 at 600 nm (about 108 cells/mL), was obtained. The bacteria were recovered from an overnight culture by centrifugation at 8000 g for 10 min. Next, 100 mL of urea (1M) was mixed with 100 mL of the bacteria culture to produce a free carbonate ion solution. The carbonate ions thus produced were combined with Fe^{2+}, Mg^{2+}, or Ca^{2+} ions (using $FeSO_4$, $MgCl_2$, and $CaCl_2$ solutions respectively) to induce $FeCO_3$, $CaCO_3$ and $CaMg(CO_3)_2$ mineral precipitation according to equations 3-4:

$$FeSO_{4\,(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow FeCO_3\,(s) \quad (3)$$

$$CaCl_2/MgCl_{2\,(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CaMg(CO_3)_2(s) \quad (4)$$

The characteristics of the reagents used are listed in Table 1.

Table 1. Chemical reagents used.

Reagents	Molarity	Cation:Carbonate Ratios	
$FeSO_4 \cdot 7H_2O$	1M	Fe^{2+}: CO_3^{2-}	1:1
$CaCl_2$/ $MgCl_2$	1M	Mg^{2+}/Ca^{2+}: CO_3^{2-}	1:1

2.2 SEM and XRD Analysis

Selected carbonate samples were analysed using various techniques including scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD). SEM was used to examine the size, shape, and arrangement of mineral crystals. To ensure good conductivity, the dry powder specimens were coated with gold before SEM testing. During these tests, we applied accelerating voltages between 2 and 10 kV. Additionally, XRD was employed at 30 kV and a 30 mA current to identify the mineral type.

2.3 Soil treatment and triaxial testing

The soil used in this study was clean silica sand of a particle size distribution shown in Figure 1, a uniformity coefficient of 2.74, a specific gravity of 2.65, and maximum and minimum void ratios of 0.90 and 0.57, respectively.

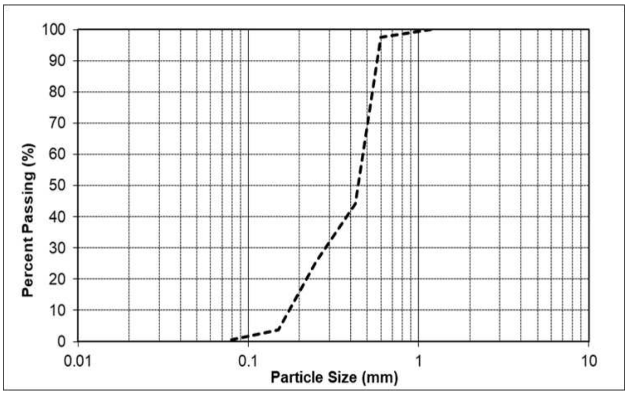

Figure 1. Particle size distribution of silica sand.

To conduct triaxial tests, cylindrical specimens of 10cm length and 5cm diameter were prepared by combining sand with a 15% content of carbonate minerals (specifically, $FeCO_3$ and $CaMg(CO_3)_2$) in accordance with ASTM D2166 standards. In some specimens 2% nanoclay was also introduced into the carbonate mixture. The specimen preparation procedure is presented in Table 2. After allowing the specimens to cure for 7 days, consolidated drained triaxial tests (CD) were performed on the treated samples following ASTM D7181 guidelines with a triaxial cell pressure of 100 kPa. All experiments were carried out in triplicate under both dry and fully saturated conditions respectively.

Table 2. Properties of sample preparation.

Sample NO.	Carbonate mineral (15%)	Nano -clay (%)	W (%)	γ (g/cm^3)
D15	Dolomite	0	10	1.98
D15+nano2	Dolomite	2	10	2
S15	Siderite	0	10	1.98
S15+nano2	Siderite	2	10	2

3 RESULTS AND DISCUSSION

3.1 Carbonate mineral production

Figure 2 shows the formed carbonate minerals. $FeCO_3$ particles exhibit a polycrystalline, spherical shape with sizes ranging from 0.5-2 µm (Figure 2 (a)). Conversely, $Ca\text{-}Mg(CO_3)_2$ crystals have a botryoidal shape, with sizes ranging from 5-16 µm (Figure 2(b)). The XRD analysis confirms the presence of $FeCO_3$ as siderite and $CaMg(CO_3)_2$ as dolomite (Figure 3).

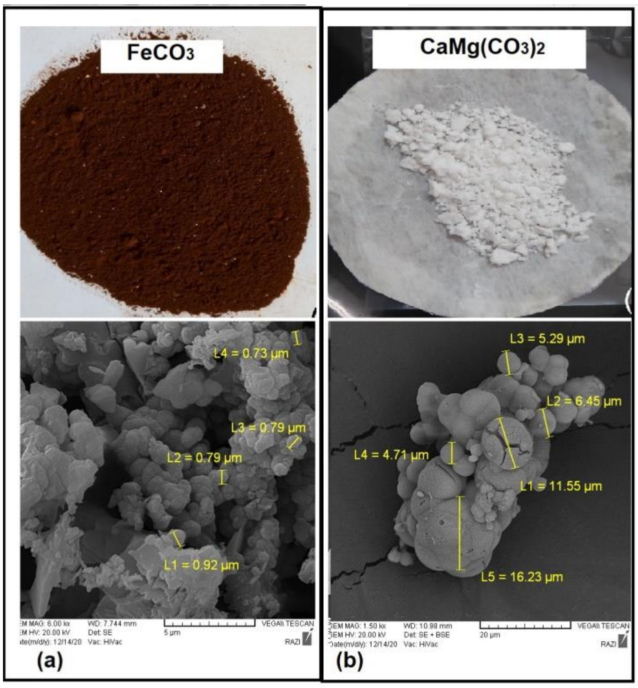

Figure 2. Macro and microstructure of carbonates.

3.2 Triaxial Compressive Strength (CD)

Figure 4 presents the stress-strain behaviour of samples treated with carbonates in a triaxial test conducted under dry conditions (CD). As illustrated, the samples treated with siderite exhibited greater strength compared to those treated with dolomite. Furthermore, samples treated with a combination of carbonate minerals and nanoclay displayed even higher strength when compared to the other treatments, with the highest strength recorded at 525 kPa observed in the sample treated with siderite and nanoclay. Additionally, the specimens treated with siderite and nanoclay were more ductile than specimens treated solely with siderite.

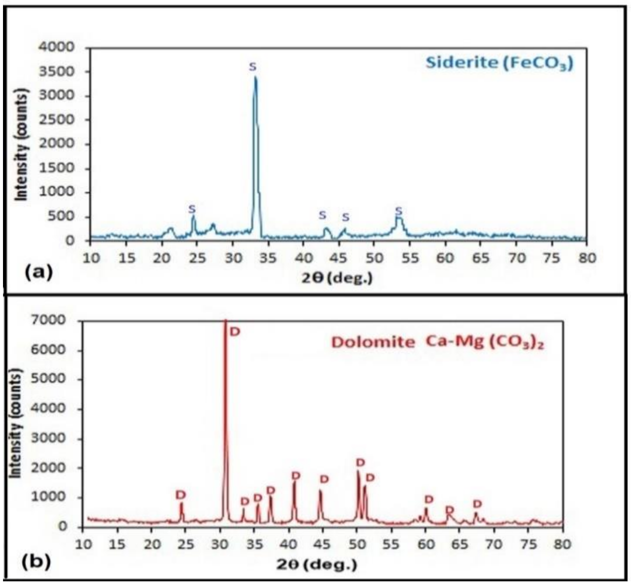

Figure 3. XRD analysis of carbonate minerals (a) Siderite, and (b) Dolomite.

The results of the triaxial test conducted under saturated conditions closely resembled those obtained under dry conditions (Figure 5). Strengths de-creased by 5% to 15% for all saturated specimens, compared to those of dry specimens; the highest strength recorded under saturated conditions was approximately 464 kPa, in the specimens treated with siderite and nanoclay. The secant modulus E_{50} of specimens decreased with the addition of nanoclay (Figure 6).

4 CONCLUSION

In this study, microbially induced carbonate preci-pitation was used to generate free carbonate ions (CO_3^{2-}). Different carbonate minerals were formed by introducing Fe^{2+}, Mg^{2+}, and Ca^{2+} ions into CO_3^{2-} solutions, resulting in the precipitation of siderite ($FeCO_3$) and dolomite ($CaMg(CO_3)_2$). Scanning electron microscopy (SEM) analysis revealed that siderite had a polycrystalline, spherical morphology ranging from 0.5 to 2 µm, while dolomite displayed a botryoidal shape ranging from 5 to 16 µm.

Consolidated drained triaxial tests (CD) were conducted on treated silica sand samples with siderite and dolomite carbonate cements (15%) as well as nanoclay (2%), under both dry and saturated conditions. The findings indicated that specimens treated with siderite had higher strengths compared to those treated with dolomite in both dry and saturated conditions. The addition of nanoclay resulted in further strength increase, with the highest recorded strength at 525 kPa observed in specimens treated with siderite and nanoclay. Nanoclay-treated samples had a reduced brittleness and can be advantageous for soil improvement.

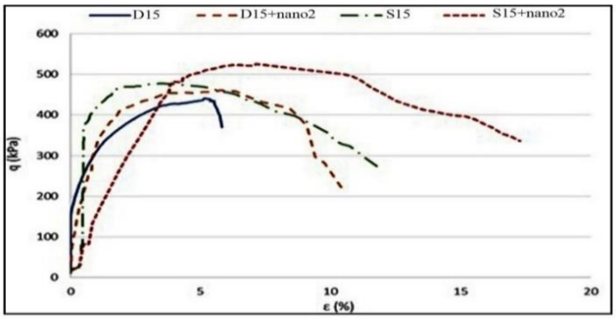

Figure 4. Stress-strain curves of dry specimens treated with 15% siderite, 15% dolomite and 2% nanoclay.

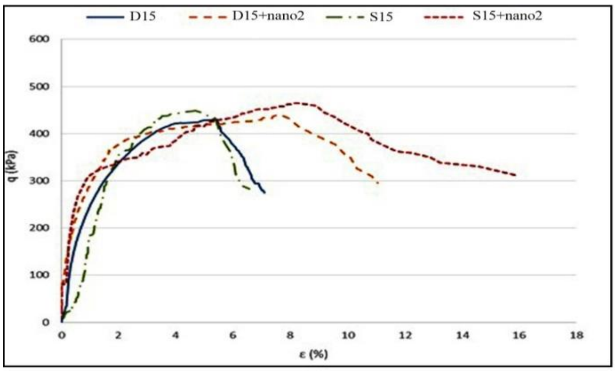

Figure 5. Stress-strain curves of saturated specimens treated with 15% siderite, 15% dolomite & 2% nanoclay.

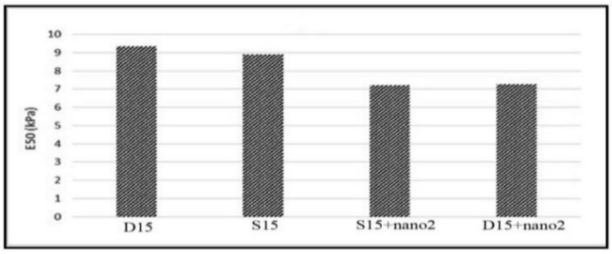

Figure 6. E_{50} variation for treated samples.

ACKNOWLEDGEMENTS

The research on this topic carried out by Dr Keykha at London South Bank University is linked to the UKRI-funded MSCA-PF project COSMIC (Grant EP/Y029607/1).

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