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Enhancing Portland cement resistance against sulfate attack in soil stabilization using CO_2-induced carbonate minerals

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ABSTRACT: In line with net carbon zero targets, this study used CO_2-induced carbonate minerals as a partial replacement for Portland Cement (PC) to enhance sand soil stabilisation and increase its durability against sulfate attack. Initially, various carbonate minerals, including siderite ($FeCO_3$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and ankerite ($CaFe(CO_3)_2$), were synthesised through a CO_2 capture process, and combined with 10% PC at a dosage of 15% (by dry soil mass) as sand soil stabilisers. Unconfined Compressive Strength (UCS) tests were conducted on the stabilised sand specimens after 28 days of curing. Subsequently, the treated specimens were exposed to a 5% Na_2SO_4 solution for three months to evaluate their durability under sulfate attack. The results showed that incorporating carbonate minerals into the PC mixture considerably enhanced the UCS and durability of the stabilised soil. Namely, the cement-siderite treated sand had a UCS of 1215 kPa, compared to approximately 845 kPa for sand treated with PC alone. Other combinations of carbonate minerals and PC showed slightly lower or similar performance, likely due to mineral density and their role as fillers. All carbonate minerals greatly improved the resistance of treated sand to sulfate attack, as all PC-carbonate treated specimens remained intact after sulfate exposure, whereas PC-treated samples were damaged. XRD analysis showed that the formation of ettringite due to sulfate was similar across PC and PC- carbonate treated samples. However, the new mineral phases, such as goethite, ferrosilite, calcium sulfate hydrates, and hematite, within the cement matrix, led to an enhanced durability in the carbonate-treated samples. The minerals $CaCO_3$ and $CaMg(CO_3)_2$ primarily helped to raise the pH, buffering the system against acidification from sulfate exposure. In contrast, $FeCO_3$ and $CaFe(CO_3)_2$ improved the microstructure by increasing density and reducing permeability, thereby limiting sulfate ingress and demonstrating their beneficial effects.

KEYWORDS: CO_2 – induced carbonate mineral precipitation, Portland cement, Sulfate attack, Sand soil improvement.

1 INTRODUCTION

Soil stabilisation is critical in geotechnical engineering, aiming to improve the engineering properties of soil such as strength, stiffness, permeability, and durability. This is essential for supporting various civil infrastructure projects, including roads, foundations, and embankments. Traditional soil stabilisation techniques commonly use Portland cement (PC) as a binding agent. While effective, the production of PC is energy-intensive and contributes significantly to greenhouse gas emissions. To reduce adverse environmental effects, significant efforts are made for the development of more sustainable soil stabilisation materials, i.e., cost-effective, energy-efficient, and durable, offering a reliable performance in terms of soil engineering characteristics, minimal maintenance needs, and ideally incorporating a high proportion of recycled content to further enhance their environmental sustainability (Kamei et al., 2018).

Various strategies have been proposed to achieve this goal, such as partially or fully substituting PC with materials such as ground granulated blast furnace slag (Eyo et al., 2020), pumice powder (Çadır and Vekli, 2022), volcanic ash, paper sludge ash (Mavroulidou, 2018), and palm oil fuel ash (Mujah et al., 2015). This study proposes instead the use of carbonate minerals, synthesised by CO_2 absorption, in conjunction with PC. The minerals can be introduced into the soil either as a priorly produced binder or precipitate within the soil matrix through microbially induced carbonate precipitation (MICP) or, alternatively, CO_2-induced carbonate precipitation (CICP) (Keykha et al., 2017, 2021; Romiani et al., 2021). The latter approach directly synthesises substantial amounts of carbonate minerals ex situ or in situ and can contribute to CO_2 mitigation, as it can sequester captured industrial CO_2.

2. MATERIALS AND METHODS

2.1 *CO_2- induced carbonate production*

Carbonate minerals were synthesised using CO_2 from an industrial gas cylinder, along with sodium hydroxide (NaOH), and calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), or ferrous chloride ($FeCl_4$). To generate free carbonate ions (CO_3^{2-}), CO_2 gas was bubbled into a 2 M NaOH solution at a flow rate of 10 mL/min over a period of 72 hours. During this process, CO_2 reacts with NaOH to produce sodium carbonate (Na_2CO_3), as shown in Equations 1–3. Carbonate minerals are then formed by adding various metal ions to the carbonate-rich solution. This leads to the precipitation of minerals such as $FeCO_3$, $CaCO_3$, $MgCO_3$, $CaMg(CO_3)_2$, and $CaFe(CO_3)_2$, according to Equations 4–8.

The minerals precipitated according to this process were collected using filter paper and dried to a powder form.

$$CO_2 + NaOH + 2H_2O \rightarrow NaHCO_{3\,(aq)} \quad (1)$$

$$NaHCO3\,(aq) + NaOH\,(aq) \rightarrow \quad Na2CO3\,(aq) \quad (2)$$

$$Na_2CO_3 \rightarrow 2Na^{+}_{\,(aq)} + CO_3^{2-}{}_{(aq)} \quad (3)$$

$$FeCl_{2\,(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow FeCO_3\downarrow \quad (4)$$

$$CaCl_{2\,(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CaCO_3\downarrow \quad (5)$$

$$MgCl_{2\,(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow MgCO_3\downarrow \quad (6)$$

$$CaCl_{2\,(aq)} + MgCl_{2\,(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CaMg(CO_3)_2\downarrow \quad (7)$$

$$CaCl_{2\,(aq)} + FeCl_{2\,(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CaFe(CO_3)_2\downarrow \quad (8)$$

2.2 *Experimental procedures*

The silica sand used had a particle size distribution (PSD) shown in Figure 1(a), a uniformity coefficient (C_u) of 2.72 and a coefficient of curvature (C_c) of 0.9, classifying it as SP (poorly graded sand) according to ASTM D2487 (ASTM, 2006). It had a specific gravity of 2.66, and maximum and minimum void ratios of 0.9 and 0.58, respectively. Samples were prepared by mixing 15% carbonate minerals and 10% PC with approximately 15% water, based on prior mix optimisation. The mixture was compacted in five layers into a split moulds of 50 mm in diameter and 100 mm height to produce uniform specimens, achieving a dry density between 1.9 and 2 g/cm³, as per Standard Proctor Test (ASTM 2021). Two sets of specimens were prepared for curing: one group was cured in a water bath for 28 days, while the other was immersed in a 5% sodium sulfate (Na_2SO_4) solution for a curing period of 3 months. Unconfined compressive strength (UCS) tests were performed on moist specimens (ASTM, 2016). After UCS testing, fragments from the specimens were cured in sulfate solution and then analysed by XRD. Figure 1(b) shows a schematic overview of the experimental process

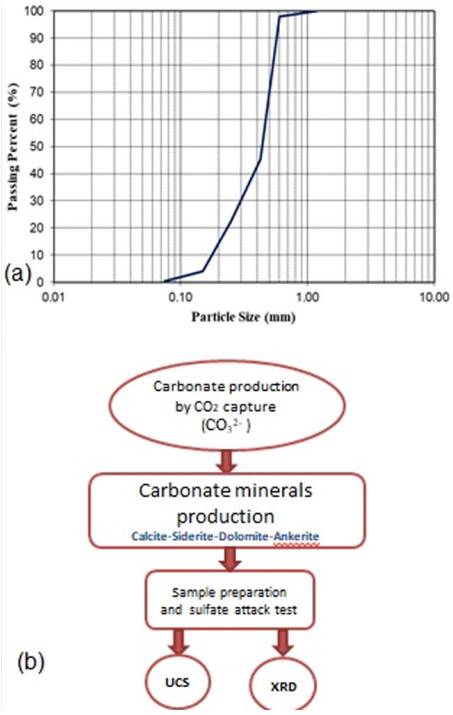

Figure 1. PSD of sand (a) and experimental procedure (b).

3. RESULTS AND DISCUSSION

3.1 *CO_2- induced carbonate production*

Figure 2 shows the SEM photos of carbonate minerals produced using the CO_2-induced precipitation process. The morphology is consistent with the formation of siderite ($FeCO_3$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and ankerite ($CaFe(CO_3)_2$) (Keykha et al., 2023), also attested in the XRD analysis.

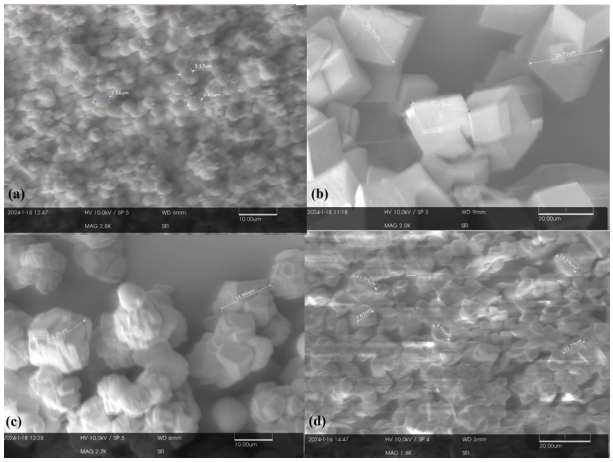

Figure 2.SEM of $FeCO_3$(a), $CaCO_3$(b), $CaMg(CO_3)_2$(c), $CaFe(CO_3)_2$(d).

3.2 *Durability to sulfate attack*

Specimens were subjected to UCS testing before and after exposure to sulfate attack respectively. As shown in Figure 3, specimens treated with only PC completely disintegrated after three months of exposure to sulphates, unlike the PC-carbonate treated specimens, showing a better durability.

Figure 3. PC and PC–carbonate-treated samples in the sulfate attack test.

Figure 4 presents the UCS results of treated samples both before and after sulfate exposure. As shown, the samples treated solely with PC had a strength of 845 kPa. For the majority of carbonate minerals, their addition caused a decline in strength, whereas siderite did not show this effect. Notably, the samples treated with PC-siderite showed a significant increase in UCS, reaching 1215 kPa. A key finding of this study is the reduced impact of sulfate attack on carbonate-treated samples. Although the UCS of these samples decreased following sulfate exposure, the results indicate they retained considerable durability after three months, whereas the PC-only samples were completely degraded despite their initially higher strength.

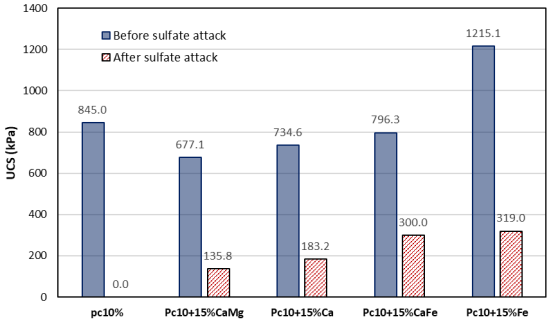

Figure 4. UCS of PC-carbonate - treated specimens.

Figure 5 illustrates the change in density of treated samples before and after sulfate attack. It is observed that samples treated with calcite and dolomite exhibit a greater reduction in density (approximately 1.84 g/cm³) compared to those treated with siderite and ankerite (around 1.93 and1.90 g/cm³).

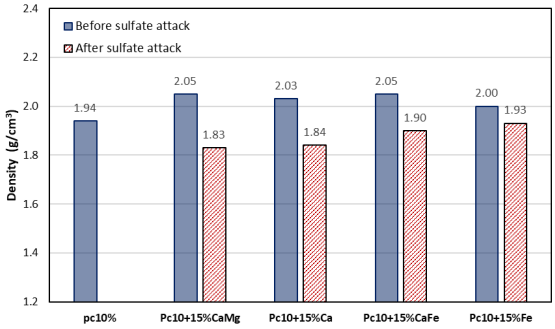

Figure 5. Density of PC-carbonate - treated specimens.

3.3 *XRD analysis*

Figure 6 shows XRD analysis results of the phases produced, including $CaCO_3$, $CaFe(CO_3)_2$, $FeCO_3$, and $CaMg(CO_3)_2$. Tables 1 and 2 present respectively their chemical composition and the quantitative analysis of these samples following sulfate attack. In the modified cement mixtures, secondary phases such as goethite, ferrosilite, calcium sulfate hydrates, and hematite were identified. These phases played a crucial role in enhancing durability and strength by reducing cracking and material degradation, effects that were not observed in the control (PC-only) sample. Interestingly, According to the XRD results, the ettringite content remained nearly constant across all samples. Early ettringite formation occurs during cement hydration through the reaction of tricalcium aluminate (C_3A) with sulfate (Na_2SO_4). This reaction is largely unaffected by the addition of carbonate minerals, when their quantities are relatively low, having a minimal impact on the availability of sulfates and aluminates required for ettringite formation. Although they may influence the development of other secondary phases, they only affect ettringite formation if used in high concentrations (Matschei et al. 2007). The increased sulfate resistance and mechanical integrity is primarily attributed to the formation of stable secondary phases such as goethite, ferrosilite, and hematite. These iron-rich phases, likely formed from reactions involving $FeCO_3$ or $CaFe(CO_3)_2$ under alkaline conditions, contribute to a denser microstructure and lower permeability, effectively limiting sulfate penetration. Ferrosilite ($FeSiO_3$) may result from the interaction between silicates and Fe-bearing carbonates, indicating the development of more compact, C-S-H-like gels that resist expansion caused by sulfate attack (Zhang et al. 2018). Additionally, iron oxides and silicates are generally more stable in a sulfate-rich environment compared to some aluminate phases that are susceptible to sulfate attack. Likewise, enstatite ($MgSiO_3$), which forms from magnesium released by dolomite, is chemically stable in sulfate-rich conditions, has low solubility, and contributes to matrix densification in a manner like C-S-H. Additionally, the added carbonates may dissolve to some extent, releasing carbonate ions (CO_3^{2-}) into the pore solution. This helps buffering the pH of the cement matrix, so that it does not become too acidic due to sulfate attack reactions (Matschei et al. 2007). Stable sulfate-containing compounds such as gypsum or monosulfate may form and act as buffers, reducing the risk of delayed ettringite formation, which typically leads to expansion and cracking. Ultimately, the consistent levels of ettringite observed across all samples are due to its dependence on the inherent sulfate and aluminate content of PC, rather than the carbonate additives. The improved durability is instead attributed to the generation of supplementary, stable mineral phases that strengthen the cement matrix and reduce its susceptibility to sulfate attack.

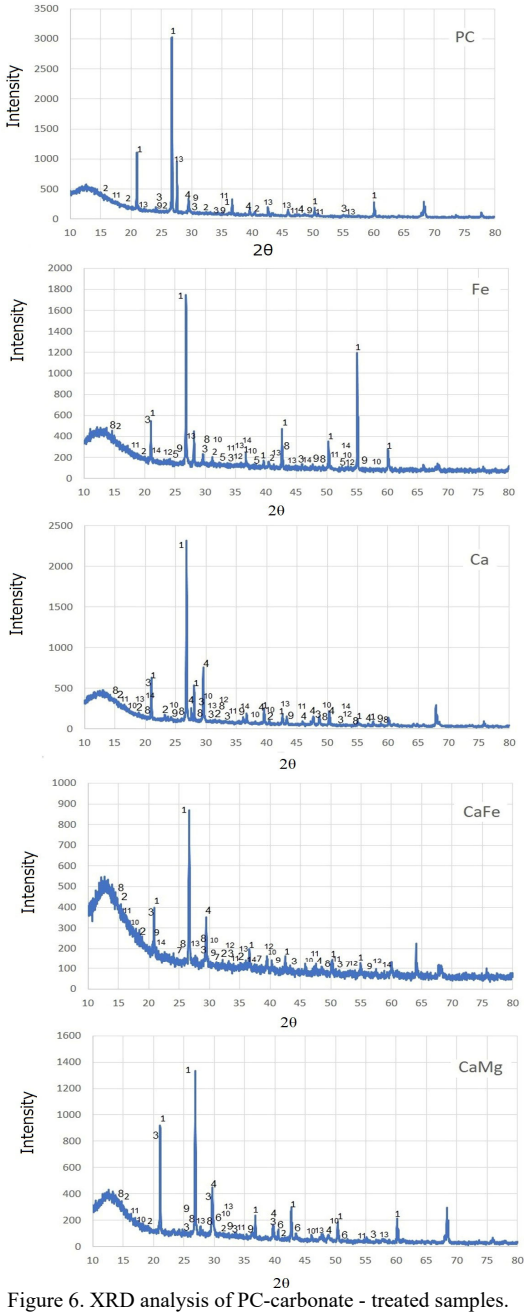

Figure 6. XRD analysis of PC-carbonate - treated samples.

Table 1. Chemical compositions of PC-carbonate - treated samples.

COD	Name	Chemical com.
1	Quartz	SiO_2
2	Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$
3	Gypsum	$CaSO_4$
4	Calcite	$CaCO_3$
5	Siderite	$FeCO_3$
6	Dolomite	$CaMgCO_3$
7	Ankerite	$CaFeCO_3$
8	CSH	Calcium Silicate-Hydrate
9	CSA	Calcium Sulfate Hydrate ($CaSO_4\cdot xH_2O$)
10	Calcium Silicate Hydroxide	Ca_2SiO_3 (OH)2
11	Portlandite	$Ca(OH)_2$
12	Hematite	Fe_2O_3
13	Ferrosilite/ enestatite	$FeSiO_3$/ $MgSiO_3$
14	Goethite	FeOOH

Table 2. Phase percentage of PC-carbonate - treated samples.

COD	Name	Pc	Pc+ Fe	Pc+ Ca	Pc+ CaFe	Pc+ CaMg
1	Quartz	66	52	56	58	49
2	Ettringite	1.3	1.2	0.9	1.1	1
3	Gypsum	1.1	5	0	8.4	10
4	Calcite	20	0	31	3	5
5	Siderite	0	5	0	0	0
6	Dolomite	0	0	0	0	16
7	Ankerite	0	0	0	10	0
8	CSH	0	6	1	1.8	6.1
9	CSA	2.6	0.65	5.5	0.8	0.5
10	Calcium Silicate Hydroxide	0	1.1	0	0.6	0.3
11	Portlandite	1.3	1	0.25	0.4	0.6
12	Hematite	0	.08	0.5	0.9	0.2
13	Ferrosilite/ enestatite	2.5	7.5	3.5	5.7	3.6
14	Goethite	0	3.5	1.8	3.5	0

4. CONCLUSIONS

This study used CO_2-induced carbonate minerals as a partial replacement for Portland Cement (PC) to enhance sand soil stabilisation and increase its durability against sulfate attack. Initially, various carbonate minerals, including siderite ($FeCO_3$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and ankerite ($CaFe(CO_3)_2$), were synthesised through a CO_2 capture process, and combined with 10% PC at a dosage of 15% (by dry soil mass) as sand soil stabilisers.

The results demonstrated that the combination of PC and carbonate materials, especially siderite, improved UCS and increased the treatment durability against sulfate attack.

XRD analysis revealed that the formation of ettringite remained relatively consistent across all samples. However, the addition of carbonate mineral additives led to the formation of secondary phases such as goethite, ferrosilite, calcium sulfate hydrates, and hematite within the cement matrix. These phases played a key role in enhancing durability and strength by minimising cracking and material degradation under sulfate attack. Among the additives, $CaCO_3$ and $CaMg(CO_3)_2$ primarily contributed to increasing the pH, helping to buffer the system against acidification caused by sulfate exposure. On the other hand, $FeCO_3$ and $CaFe(CO_3)_2$ improved the microstructure by increasing density and reducing permeability, thereby limiting sulfate ingress. The enhanced durability is thus attributed to the formation of stable mineral phases that reinforce the cement matrix and reduce its vulnerability to sulfate-induced damage.

5. ACKNOWLEDGEMENTS

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