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Carbonating magnesia for soil stabilization

Yaolin Yi, Martin Liska, Cise Unluer, and Abir Al-Tabbaa

Abstract: This paper investigates the potential for carbonating reactive magnesia (MgO) to serve as a more sustainable soil stabilization method by providing rapid and significant strength development of the stabilized soil through absorbing substantial quantities of CO₂. Gaseous CO₂ was forced through laboratory-prepared reactive MgO-treated soil samples in a triaxial cell set-up, and their resulting mechanical and microstructural properties were investigated using unconfined compressive strength, X-ray diffraction, and scanning electron microscopy. The results showed that adequately carbonated MgO-treated soils could, in a few hours, reach a similar strength range to corresponding 28 day Portland cement (PC)-stabilized soils. Hydrated magnesium carbonates, namely nesquehonite and hydromagnesite–dypingite, were the main products of the carbonated MgO in the soil, and were responsible for the significant strength development.

Key words: soil stabilization, reactive MgO, carbonation, unconfined compressive strength, microstructure.

Résumé : Cet article étudie le potentiel de la magnésie réactive carbonisée (MgO) à être utilisée comme méthode de stabilisation plus durable des sols, en permettant un développement de résistance rapide et significatif du sol stabilisé par l'absorption de quantités substantielles de CO₂. Du CO₂ sous forme gazeuse a été forcé à travers des échantillons de sol traités au MgO préparés en laboratoire et placés dans une cellule triaxiale, et les propriétés mécaniques et microstructurales résultantes ont été évaluées à l'aide de la résistance à la compression non confinée, la diffraction des rayons-x et la microscopie électronique à balayage. Les résultats ont démontré que les sols traités au MgO et adéquatement carbonisés peuvent atteindre, en quelques heures, des valeurs de résistance similaires à un sol stabilisé avec du CP après 28 jours de cure. Les carbonates de magnésium hydratés, dont la nesquehonite et l'hydromagnésite–dypingite, sont les principaux produits de la carbonatation du MgO dans le sol et sont responsables du développement significatif de la résistance. [Traduit par la Rédaction]

Mots-clés : stabilisation du sol, MgO réactive, carbonatation, résistance en compression non confinée, microstructure.

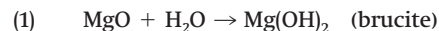
Introduction

Portland cement (PC) is the most widely and commonly used binder in soil stabilization (Sherwood 1993; Bruce 2001; Moseley and Kirsch 2004). The primary stabilization mechanism in soils is through the hydration of the cement, leading to the formation of calcium silicate hydrates (C-S-H), calcium aluminate hydrates (C-A-H) and calcium aluminium silicate hydrates (C-A-S-H), which are responsible for the main strength development, as well as Portlandite (Ca(OH)₂), which in turn may react, much slower, with any clay minerals present leading to the formation of more of the hydration products above, contributing to the longer-term strength (Hausmann 1990). The unconfined compressive strength (UCS) of PC-stabilized soils is the key design parameter for ground improvement applications, and is typically between 0.1–5.0 MPa (Bruce 2001; Moseley and Kirsch 2004), varying significantly between countries and for different applications.

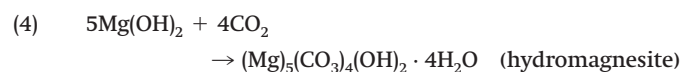
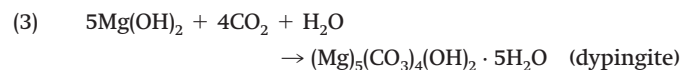
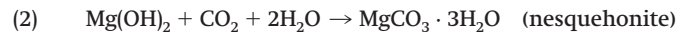
However, there are significant environmental impacts associated with the production of PC, in terms of high energy consumption and CO₂ emissions (~0.95t CO₂/t PC), leading to a range of global initiatives for the development of alternative cements (WBCSD 2002). One recent development is the family of reactive magnesia (MgO) cements (Harrison 2008). Reactive MgO is generally calcinated from magnesite (MgCO₃) at temperatures of around 700–800 °C, and should not be confused with deadburned MgO manufactured at a temperature higher than 1400 °C (Shand 2006). The energy consumption during reactive MgO production is much lower than that of PC (manufactured

at approximately 1450 °C) and the renewable energy sources can be used.

Extensive research has been conducted at the University of Cambridge since 2004 into reactive MgO cements (e.g., Vandeperre and Al-Tabbaa 2007; Liska and Al-Tabbaa 2008, 2009; Vandeperre et al. 2008a, 2008b; Liska 2009; Liska et al. 2008, 2012a, 2012b; Unluer 2012). The details and findings have been compiled into a book chapter (Al-Tabbaa 2013) and those relevant are summarized here. Reactive MgO hydrates much faster than deadburned MgO to form brucite:



Brucite has a very limited binding ability (Liska 2009). However, under appropriate conditions, brucite will carbonate (provided the structure is porous enough for gaseous CO₂ to penetrate through it) to form one or more of the following hydrated magnesium carbonates:



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The formation of these carbonates is influenced by several factors, such as temperature and CO_2 partial pressure, as well as the composition and characteristics of the original MgO (Davies and Bubela 1973; Königsberger et al. 1999; Marini 2007; Xiong and Lord 2008; Liska 2009). The hydration of MgO and carbonation of brucite are expansive reactions and the solid volume of MgO increases by 3.8–6.7 times at the end of carbonation, which significantly fills available pores. These hydrated magnesium carbonates also form well-ramified networks of massive crystals with a very effective binding ability, resulting in substantial and rapid strength increase. In porous construction blocks, they significantly outperformed PC with strengths of 200%–300% higher (Liska 2009). High levels of carbonation, including full carbonation, have been achieved in full-scale porous blocks trial production (Liska et al. 2012a, 2012b), reabsorbing most of the CO_2 generated during the decomposition of the magnesite.

This paper investigates the applicability of carbonating reactive MgO for soil stabilization to assess its technical and environmental performance in a range of conditions including soil type, soil water content (w/s), binder content and carbonation method, and to compare its performance with that of PC. This work is complemented by a set of experiments using a laboratory-scale auger to model the installation of carbonated soil-MgO deep mixed columns (Yi et al. 2010, 2013).

Materials and methods

Two model soils were used, namely a slightly clayey silty sand, consisting of 90% sharp sand, 5% kaolin clay, and 5% silica flour, and an organic clayey silt consisting of 82% silica flour, 15% kaolin clay, and 3% peat. The sharp sand (obtained from Ridgeons, Cambridge, UK) had a D_{50} of 0.8 mm and coefficient of uniformity of 4.3. The kaolin clay and reactive MgO were obtained from Richard Baker Harrison, Ilford, UK; the silica flour was obtained from David Ball Group, Cambridge; and the peat was obtained from Scotsdales Garden Centre, Cambridge. The MgO and PC (CEM I, BSI (1990), obtained from Castle Cement, UK) were applied at either 5% or 10% dry content to the soils. The chemical compositions of some of these materials are presented in Table 1. The silt had a liquid limit of 32% and plastic limit of 24%. The dry soil components were initially homogenized in a bench-top mixer after which water was added and the mixing continued for further homogenization. The binder was then applied to the soils and mixed until homogenized, and the mix was then placed in cylindrical moulds, 50 mm in diameter and 100 mm in height, applying consistent moderate compaction in three layers by rodding and eliminating trapped air pockets. The samples were demoulded approximately 1 h later, weighed and placed in the triaxial apparatus and subjected to the carbonation procedures detailed below. This setting-up procedure of the samples required them to have some early strength, and samples with excessively high or low water content would be too weak to handle. Hence, only four soil water contents of between 2.5% and 10% for the sand and three between 15% and 25% for the silt were used for the samples subjected to carbonation. A subset of samples was cured in their moulds under “ambient” conditions, of $20^\circ\text{C} \pm 2^\circ\text{C}$ and $95\% \pm 3\%$ relative humidity, for 28 days.

A triaxial apparatus was used to permeate pressurized gaseous CO_2 through the samples as shown in Fig. 1. The samples were subjected to 400 kPa confining pressure and followed by upward permeation of the CO_2 at 200 kPa (gauge pressure) with the outflow tube placed underwater to detect the gas flow. Once this was observed, the outflow tap was closed two minutes later while keeping the inlet open, therefore maintaining the CO_2 pressure at 200 kPa for the designated time intervals (carbonation period), which varied from 0.5 h to 7 days. Two other CO_2 pressures of 50 and 100 kPa were also used for a selected mix for comparison purposes. An incubator with 20% CO_2 concentration at $20^\circ\text{C} \pm 2^\circ\text{C}$

Table 1. Mineralogical composition (by % wt) of the materials.

Composition	Kaolin	Silica flour	MgO	PC
CaO	0–0.3	0.01	1.2	63.6
SiO_2	45–55	99.2	1.2	13.9
Al_2O_3	30–39	0.3	0.2	10.2
Fe_2O_3	0–2	0.1	0.2	2.7
MgO	0–0.6	<0.02	97.2	0.6
K_2O	0–5	0.04	NM	0.9
TiO_2	NM	0.06	NM	0.1
SO_3	NM	NM	NM	6.9
Na_2O	0–0.3	<0.03	NM	NM

Note: NM, not measured.

Fig. 1. Triaxial cell set-up system used for soil-MgO sample carbonation.

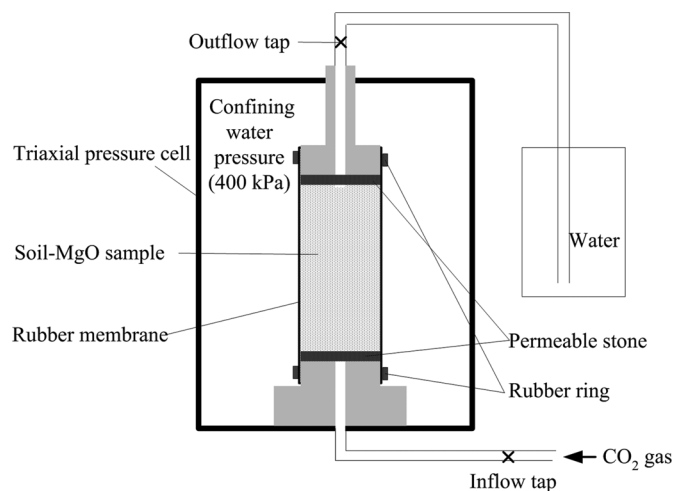
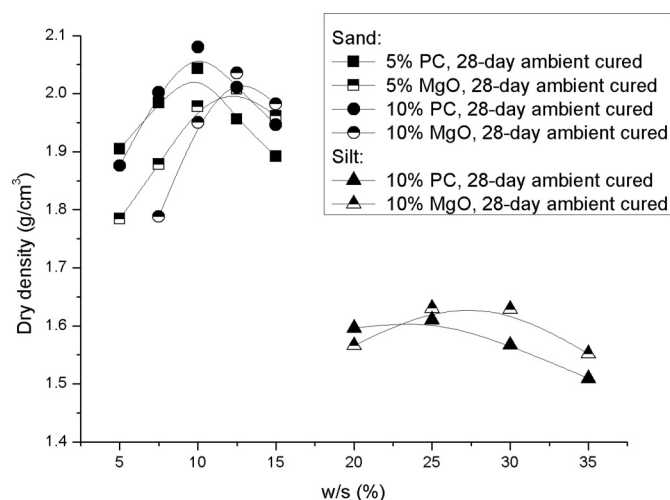


Fig. 2. Dry density versus initial soil water content (w/s) relationship.



and $95\% \pm 3\%$ relative humidity was also used for a diffusion-controlled carbonation of a selected mix again for comparison. All the samples were tested in triplicate for their unconfined compressive strength (UCS) at a constant displacement rate of 1.14 mm/min.

Microstructural analyses of selected samples, taken from the centre of the crushed UCS samples, were conducted employing X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). The XRD was performed using a powder diffractometer

Fig. 3. UCS of 28 day ambient cured MgO- and PC-stabilized soils and the highly carbonated MgO-treated soils.

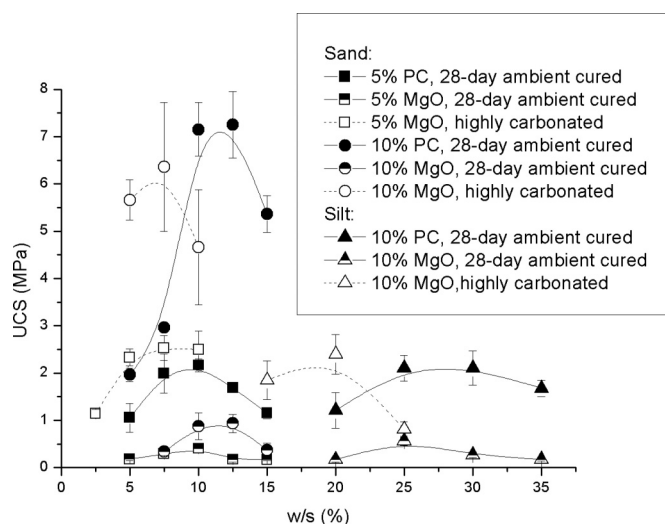
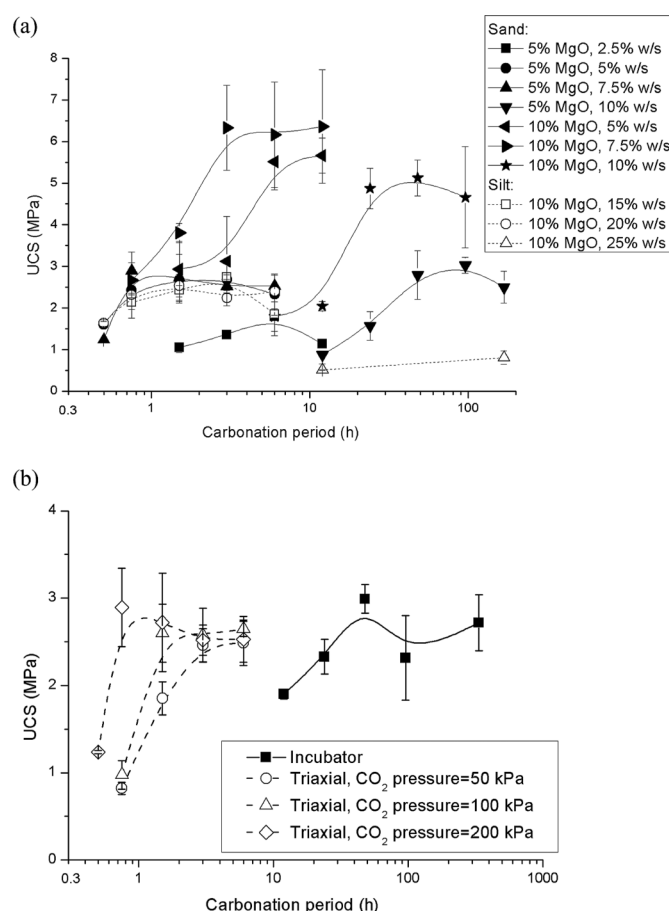
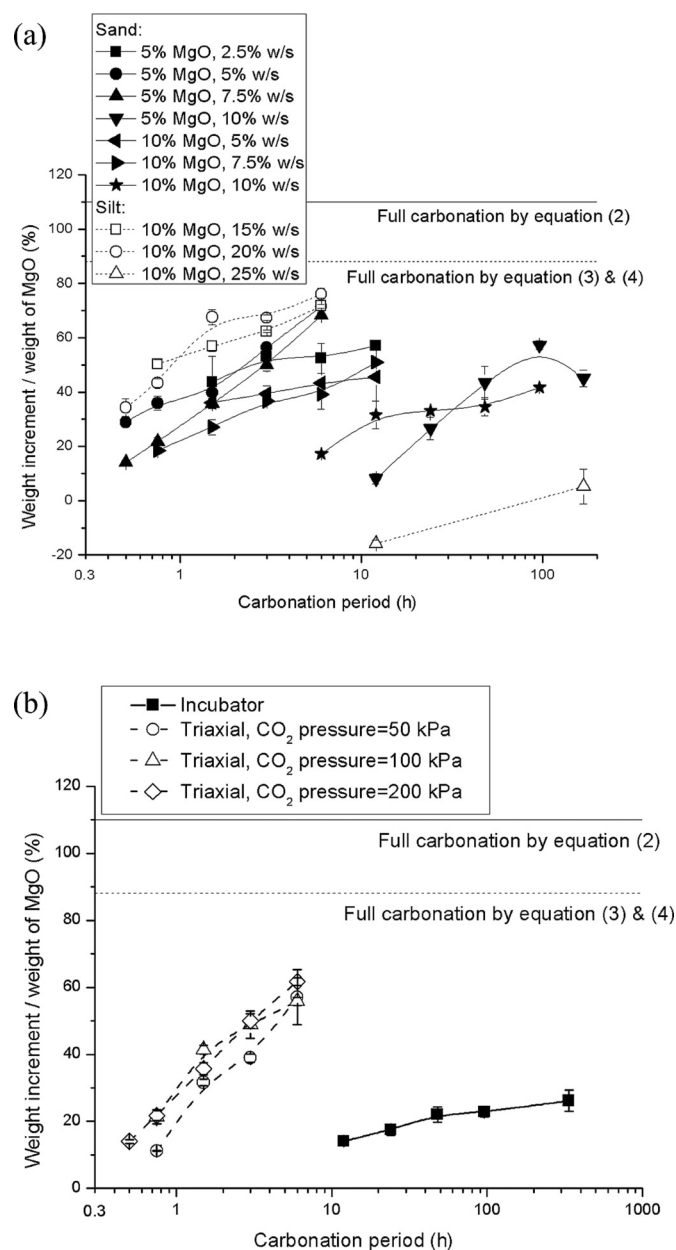


Fig. 4. UCS of the carbonated MgO-treated soil: (a) its development with carbonation period in the triaxial set-up with 200 kPa CO_2 pressure; (b) of the 5% MgO content and 7.5% w/s in the triaxial set-up with the three different CO_2 pressures as well as in the CO_2 incubator.



Bruker D8 Advance, Bruker AXS Inc., Madison, WI with a Cu $\text{K}\alpha$ source, to identify the crystalline phases in the cement-stabilized matrix and a JEOL 820 SEM equipment was employed to acquire highly magnified microimages.

Fig. 5. Percentage weight increase of the MgO: (a) in the stabilized sand and silt carbonated in the triaxial cell set-up with 200 kPa CO_2 pressure; (b) in the sand treated with 5% MgO content at 7.5% w/s carbonated in the triaxial cell set-up with three different CO_2 pressures as well as the incubator.

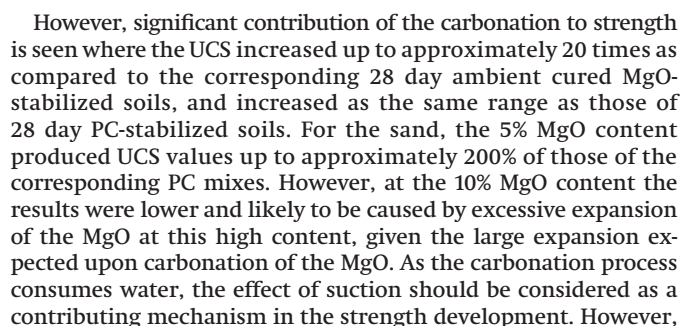


Results and discussions

Density and UCS

The dry density against initial w/s of the ambient cured PC- and MgO-stabilized soils after 28 days of curing is presented in Fig. 2, showing generally similar profiles for the same soil, with slightly higher optimum w/s for the MgO-stabilized soils than the corresponding PC-stabilized soils, linked to its rapid hydration rate. Figure 3 presents the 28 day UCS of the ambient cured MgO- and PC-stabilized soils, as well as the highly carbonated MgO-treated soils, which were carbonated in the triaxial cell with 200 kPa CO_2 for their longest carbonation periods and will be further discussed later, with the margins of error shown by the error bars. It is clear that the UCS of 28 day ambient cured MgO-stabilized soils is much lower than that of the corresponding PC-stabilized soils.

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Comparing Figs. 2 and 3 shows that for the ambient cured MgO- and PC-stabilized soils, the maximum UCS is generally consistent with the optimum dry density. However, for the carbonated soils, the maximum UCS correlate with lower w/s mixes at which the porosity was higher, which facilitated better conditions for carbonation. In the very low w/s samples, insufficient water is available, which is needed for both the hydration and carbonation processes, as in eqs. (1)–(4), while the excessive water in the high w/s samples substantially slowed down the

Fig. 8. Scanning electron micrograph of the MgO-treated sand (5% MgO content, 7.5% w/s) ambient cured for 28 days.

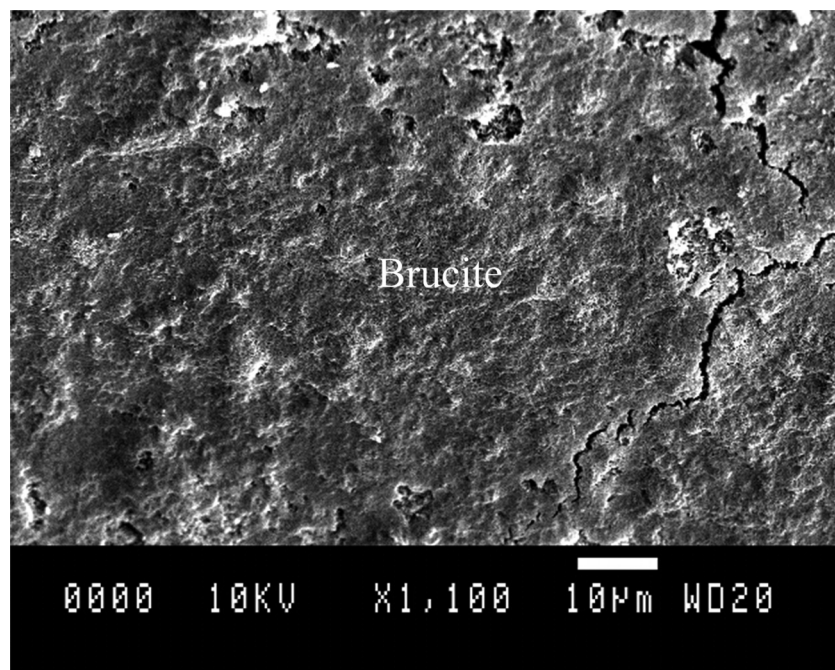
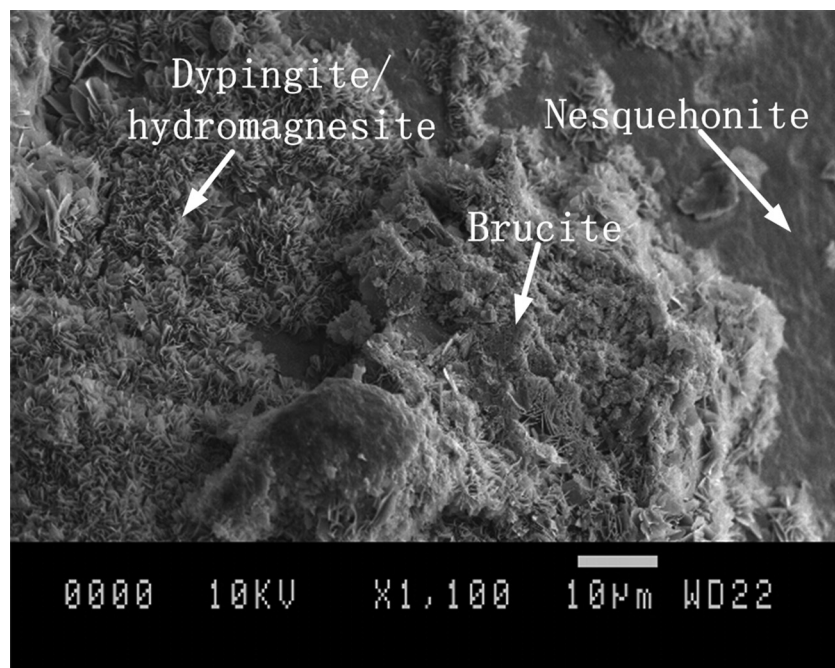


Fig. 9. Scanning electron micrograph of the MgO-treated sand (5% MgO content, 7.5% w/s) carbonated in the triaxial cell set-up with 200 kPa CO₂ pressure for 0.5 h.



transport of CO₂ within the sample and hence the carbonation process (Liska et al. 2008).

Figure 4a shows the UCS with carbonation period for the MgO-treated samples carbonated in the triaxial set-up at 200 kPa CO₂. A rapid strength increase can be seen, whereby after only 3 h the UCS of both the 5% and 10% MgO mixes were similar to those of the corresponding 28 day PC mixes. For all the mixes, an optimum UCS was reached followed by a plateau. In some cases a slight decrease was observed, although it is not clear whether a real decrease in strength occurred due to the large variability of the values. The rate of UCS development showed some dependence on

soil water content, with the highest rate being seen at 5%–7.5% for 5% MgO-treated sand, 7.5% for 10% MgO-treated sand, and 15%–20% for 10% MgO-treated silt, which were lower than the optimum w/s value in Fig. 2. These mixes provided the optimum conditions, including water and porosity, and hence facilitated the carbonation as discussed before.

Figure 4b shows that the rate of the UCS development is proportional to the CO₂ pressure for the same mix carbonated in the triaxial set-up, i.e., by halving the CO₂ pressure to 100 kPa, the carbonation period taken to achieve the same strength doubled. The samples carbonated in the incubator with minimal CO₂

Fig. 10. Scanning electron micrograph of the MgO-treated sand (5% MgO content, 7.5% w/s) carbonated in the triaxial cell set-up with 200 kPa CO₂ pressure for 6 h.

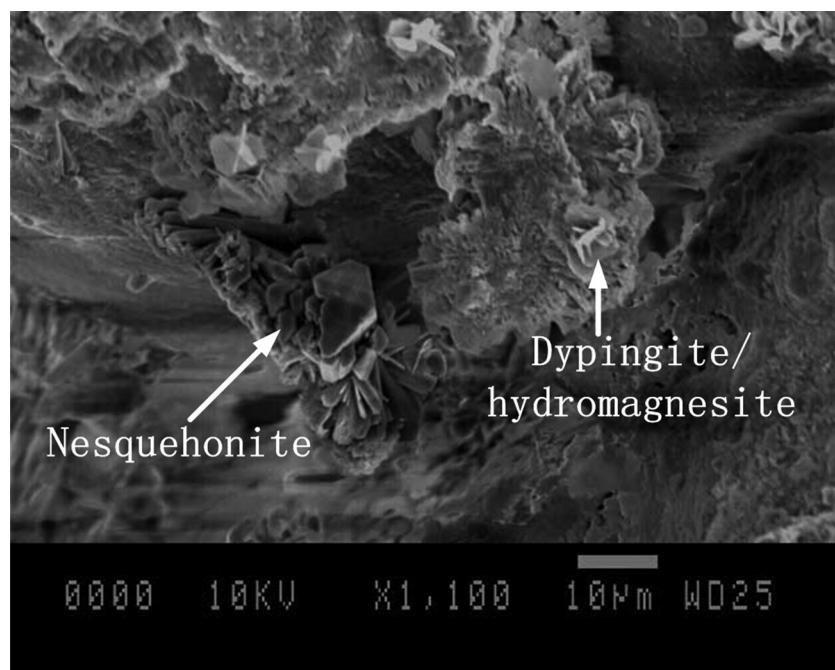
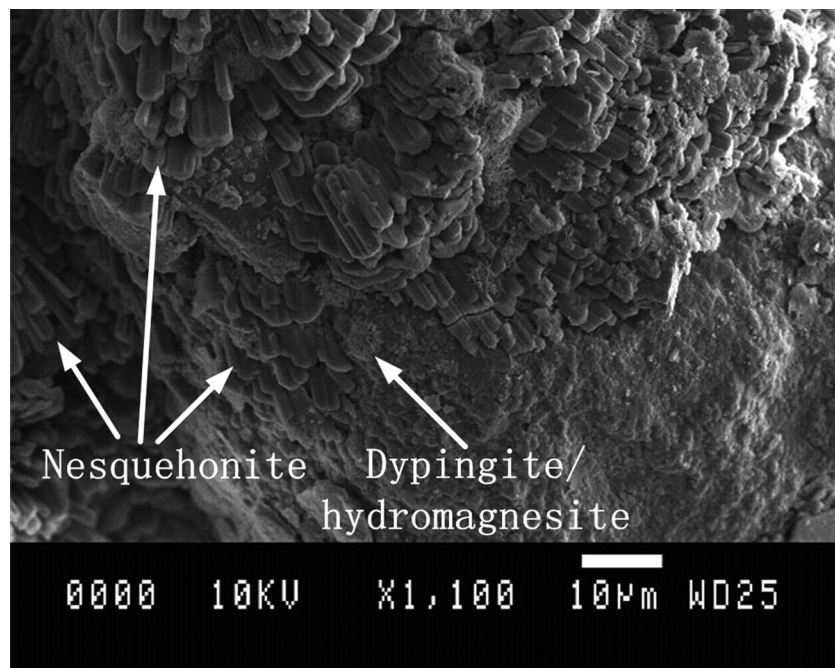


Fig. 11. Scanning electron micrograph of the MgO-treated sand (5% MgO content, 7.5% w/s) carbonated in the incubator for 7 days.



pressure (1 bar; 1 bar = 100 kPa) and at 20% concentration took two orders longer time to achieve the same strength. However, the maximum attained strength is approximately the same regardless of the CO₂ pressure applied and its concentration.

Rough quantitative assessment of the degree of carbonation

As shown in eqs. (2)–(4), CO₂ is absorbed when the hydrated magnesium carbonates are formed, which will give rise to a maximum theoretical increase in weight by 88%–110% of the total MgO content if full carbonation is achieved. The weight increase after

carbonation is shown in Fig. 5, which indicates a maximum value of up to approximately 70% increase of the MgO content, which corresponds to around 65%–80% carbonation. However, these values are likely to be underestimated as there are a number of factors which usually lead to loss in the sample weight including spalling of material during handling and loss of water due to evaporation. The samples carbonated in the incubator in particular exhibited a limited mass increase, most likely due to its more serious loss of water by evaporation. The weight increase results also show a gradual increase in mass of the samples, despite the

strength reaching a plateau at some point. This indicates that a certain level of densification, which is not necessarily at its maximum level, is sufficient to reach the maximum strength. Further carbonation will result in increased levels of densification and CO₂ sequestration, but will have no further impact on strength.

XRD and SEM

Figure 6 shows the XRD diffractograms of the 5% MgO-treated sand at 7.5% w/s ambient cured for 28 days and carbonated in the triaxial set-up with 200 kPa CO₂ for different time intervals. Evidently two strong brucite peaks and a weak MgO peak are detected for the 28 day ambient cured MgO-treated sand. For the carbonated samples, the early disappearance of the MgO peak together with weak peaks of brucite suggests the rapid hydration and carbonation of the MgO, resulting in the formation of nesquehonite and dypingite-hydromagnesite. With no other changes in the mineralogy, this correlates with the rapid and significant strength development and increase in weight.

Figure 7 shows the XRD diffractograms of four of the highly carbonated MgO-treated sands. Similar to the mix carbonated for 6 h in Fig. 6, the 5% MgO mix at 5% w/s also shows no brucite or MgO peaks, indicating that a high degree of carbonation was achieved. Although the carbonation rate was slow, the 5% MgO mix at 10% w/s achieved a high degree of carbonation after 7 days. However, for the 10% MgO mix at 7.5% w/s carbonated for 12 h, there was a clear MgO peak without brucite peaks, indicating there was not enough water left to hydrate the rest of the MgO and carbonate it. For the 10% MgO mix at 10% w/s, there were brucite peaks and a weak MgO peak, indicating that the brucite was not carbonated even after 4 days. This is due to the fact that the higher MgO content leads to higher hydration and carbonation products that filled the soil voids to a larger extent, thus slowing down the transport of the CO₂ within the sample.

Typical SEM micrographs of the 5% MgO-treated sand at 7.5% w/s ambient cured for 28 days and carbonated in the triaxial set-up with 200 kPa CO₂ for 0.5 and 6 h, as well as in the incubator for 7 days, are shown in Figs. 8–11. The 28 day ambient cured sample (Fig. 8) exhibits the porous matrix of brucite, which has a very limited binding ability due to its poorly interconnected structure (Liska 2009). All the carbonated samples (Figs. 9–11) show dense microstructures and display formations of nesquehonite and dypingite-hydromagnesite. The brucite was also observed in Fig. 9, confirming that there was only partial carbonation at 0.5 h, and then disappeared at 6 h (Fig. 10), confirming that the carbonation proceeded to a high degree.

Conclusions

Adequately carbonated MgO-treated soils could in a few hours reach a similar strength range to corresponding 28 day PC-stabilized soils. XRD diffractograms and SEM images confirmed the nesquehonite and hydromagnesite-dypingite as the main carbonation products that formed, which are responsible for the significant strength development. This work confirms that reactive MgO is promising as a rapid and sustainable stabilization binder through the sequestration of CO₂, and this method has a potential application in soil mix for ground improvement as well as contaminated soil treatment (stabilization-solidification). There is clearly a need for a much more extensive investigation into this novel method, including field-scale trials by using existing suitable equipments with some refits.

Acknowledgements

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List of symbols

- D₅₀ particle size corresponding to 50% of the grading (mm)
- w/s water in the soil to the dry soil by weight (%)