Yang, Y., Ruan, S., Wu, S., Chu, J., Unluer, C., Liu, H. and Cheng, L. (2021)
Biocarbonation of reactive magnesia for soil improvement. *Acta Geotechnica*, 16(4), pp.
1113-1125.

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Biocarbonation of Reactive Magnesia for Soil Improvement

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Abstract: This paper presents a microbial technique for soil improvement through microbially induced carbonate precipitation (MICP) as well as the incorporation of reactive magnesia cement (RMC). Influence of several parameters including the RMC, urea and water contents on MICP efficiency were investigated. The performance of RMC samples was analyzed by unconfined compressive strength and permeability measurements, further supported by microstructural analysis including SEM, XRD and TGA. RMC samples were compared with corresponding Portland cement (PC) samples as well as conventional MICP treated samples. Results indicated the formation of different types of biocarbonation phases enabled by the carbonate ions obtained from urea hydrolysis via microbial metabolism. These phases, identified as hydrated magnesium carbonates (HMCs) bridged the loose sand particles together and filled out the pores, thereby resulting in early strength development. Formation of HMCs facilitated the improvement of the mechanical performance (2.3 MPa at 28 days) and reduction of the permeability ($\sim 10^{-7}$ m/s) of the prepared mixes. The obtained findings demonstrated that the adopted MICP approach involving RMC was an effective method for soil improvement.

Keywords: Biocarbonation; microbially induced carbonate precipitation (MICP); reactive MgO; soil improvement; unconfined compressive strength; microstructure

1. Introduction

The incorporation of cement in soil is the most widely used method for soil improvement. Portland Cement (PC) is the most commonly used binder during this process due to its effectiveness (Al-Tabbaa 2003). However, the production of PC has raised significant environmental concerns due to its considerable energy consumption and CO₂ emissions, which is responsible for 5-7% of total global anthropogenic CO₂ emissions (Benhelal, Zahedi et al. 2013). This has led to the investigation of alternative binders with lower energy requirements and CO₂ emissions. Compared with PC, due to the lower temperature required for its production (750 vs. 1450 °C) and its potential to sequester CO₂, reactive magnesia (MgO) cement (RMC) has been proposed in various cement-based applications with or without PC and other pozzolans (Vandeperre, Liska et al. 2008, Unluer and Al-Tabbaa 2013, Ruan and Unluer 2017). Compared to conventional PC mixes, RMC relies on the carbonation process to gain strength and attain stiffness, instead of the hydration process. This carbonation process typically initiates with the hydration of RMC to form brucite (Mg(OH)₂), which further produces a mixture of hydrated magnesium carbonates (HMCs) upon its reaction with CO₂. Representative HMCs observed within carbonated RMC systems are nesquehonite (MgCO₃·3H₂O), hydromagnesite (4MgCO₃·Mg(OH)₂·4H₂O), dypingite (4MgCO₃·Mg(OH)₂·5H₂O) and artinite (4MgCO₃·Mg(OH)₂·5H₂O). The basis of the carbonation process is summarized in Equations (1)-(5):

Previous studies (Mo and Panesar 2012)(De Silva, Bucea et al. 2006) reported that the morphology of carbonates is the main factor that determines the final performance of binders. However, previous results show that the rate and degree of carbonation, as well as the morphology jointly commit to the final performance of RMC-based blends (Ruan and Unluer 2017). Through the carbonation process of RMC samples at 10% of CO₂, the performance of the RMC samples is comparable with the PC counterparts, which can achieve a 28-day strength of 62 MPa. Besides, by the incorporation of various types of additives such as supplementary cementitious materials (Ruan and Unluer 2017), calcined dolomite (Ruan, Liu et al. 2017, Ruan and Unluer 2018), nucleation seeds (Dung and Unluer 2017) and fibers (Ruan, Qiu et al. 2018), the performance of RMC-based blends can be significantly improved and mitigate certain environmental impacts such as global warming and ecotoxicity (Ruan and Unluer 2016, Mo, Zhang et al. 2017, Ruan and Unluer 2017). Meanwhile, as an expansive process, the introduction of an appropriate amount of reactive MgO could reduce the porosity of binders, which improve their overall mechanical performance (Mo, Deng et al. 2010, Qureshi and Al-Tabbaa 2016). However, it is difficult to control the expansion process when a large amount of reactive MgO was used, and it is notable that in porous blocks, 10% of MgO content is enough to present excellent mechanical properties under the accelerated carbonation process while eliminating the expansion problem (Unluer and Al-Tabbaa 2013). This is mainly attributed to the formation of HMCs as the carbonate crystals that

can serve as bonding material and as a pore-filling material to reduce the overall pore volume, resulting in a dense network structure of RMC mixes (Ruan and Unluer 2017).

Recent studies based on the Microbially Induced Carbonate Precipitation (MICP) process highlighted the crack healing ability of this process within RMC-based mixes (Ruan, Qiu et al. 2019). This was supported by the formation of HMCs resulting from the carbonation process, which healed the cracks within RMC-based samples. During the MICP process, urease-producing bacteria decomposes urea to yield two moles of ammonia and one mole of CO₂. This method can also be used for the microbial deposition of CaCO₃ in a calcium-rich environment (Ivanov and Chu 2008, Van Paassen 2009, DeJong, Mortensen et al. 2010). Similarly, the MICP process can also combine magnesia-bearing materials, leading to the precipitation of HMCs, in line with Equations (6) and (8) (Ruan, Qiu et al. 2019). The schematic presentation of the biocarbonation process is shown in Fig. 1.

Figure 1: Schematic representation of the biocarbonation process

Unlike accelerated carbonation that requires a high concentration and pressure of CO₂ for the curing of RMC-based mixes, the MICP approach together with the addition of RMC adopted in this study eliminated the use of gaseous CO₂ as carbonation source, which is more feasible in practice. Furthermore, most of the studies reported so far using the MICP process involved the calcium-based systems and the resultant precipitation is calcium carbonate mainly. In view of this, compared to the conventional MICP process, RMC-based MICP process does not require any soluble calcium sources as an external ingredient, which in turn increases the cost-effectiveness of this approach. Therefore, to our best knowledge, this research is the first in literature to investigate the feasibility of the microbial carbonation of RMC-based blends used in the area of soil improvement. The relatively lower pH (9-10) of carbonated RMC-based mixes can provide a suitable environment for the bacteria in the MICP process (Yang, Chu et al. 2020), thus the microbial carbonation via the MICP process could serve as a promising solution in terms of soil improvement.

This paper focuses on the performance of biocarbonated sand within RMC-based mixes. Several parameters, including the MgO and urea contents controlling the MICP process, as well as the water content, were investigated. The performance of biocarbonated sand with different MgO contents was assessed at different durations through the measurement of unconfined compressive strength and permeability. The extent of biocarbonation and the morphology of the resulting phases were evaluated, which determined the mechanical performance and microstructural development of the prepared samples. Scanning electron microscopy (SEM) was used to observe the microstructural development of the prepared samples. Thermogravimetric analysis (TGA) was employed to quantify the carbonate phases that formed during the biocarbonation process. The presence and the amount of biocarbonation products within each sample were further explored with the x-ray diffraction (XRD).

2. Materials and Methodology

2.1 Materials, mix composition and sample preparation

The reactive magnesia cement (RMC) used in this study was obtained from HCS Scientific & Chemical Pte Ltd (Singapore). The chemical composition and physical properties of RMC as provided by the supplier is listed in Table 1. Pure Ottawa sand with a mean grain size of $D_{50} = 0.4$ mm supplied by SNL (France) was used to form the aggregate profile in preparing of sand columns.

Urease-producing bacteria (UPB) isolated from local activated sludge, identified as *Bacillus Sporosarcina pasteurii* via genetic analysis, was used for biocarbonation. Bacteria culture was inoculated at a ratio of 1 ml/100ml into growth medium and cultivated under aerobic sterile conditions. The cultivation medium consisted of 10 g/L ammonia chloride, 20 g/L yeast extract and 0.01 g/L nickel chloride, at pH = 9 set by NaOH. Cultivation was conducted at room temperature (25 ± 1 °C) with an orbital shaker at a speed of 300 rpm, then harvesting after 36 hours of cultivation. The originally harvested bacterial culture had an optical density (OD_{600}) of bacterial culture about 3 ± 0.1 , and the urease activity was about 15 ± 0.2 U/ml (1U = 1 μ mol urea hydrolyzed per minute). Industrial granular urea particles were used for MICP process to produce carbonate for biocarbonation. It is worth mentioning that bacterial culture should be used within 10 days and stored at 4°C prior to use.

Table 1: Chemical composition and physical properties of RMC

Chemical Composition (%)					Physical Properties	
MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Specific gravity (g/cm ³)	Dry density (g/cm ³)
97.75	0.85	1.13	0.12	0.15	3.0	3.58

2.2 Biocarbonation of RMC samples

PVC columns with a dimension of 50 mm in diameter and 100 mm in height were prepared to cast RMC samples. Each column was placed with a piece of glossy film paper closed to the inner wall. A fitting cap was settled at the bottom for ease of demolishing. A total of 350 g dry

Ottawa sand were used as aggregate for each column, this led to the prepared RMC samples having about 65 cm³ of void volume. RMC-based mixes were prepared by mixing the dry components first, followed by adding bacterial culture with solid urea dissolved to the dry mix. The prepared mixes were then cast into PVC columns, consolidating by a vibrating table and trowel finished. All samples were demolded after 24 h and cured in the air (25 ± 1 °C, 75 ± 5 RH, ambient CO₂) to gain strength for up to 28 days. To study the effect of water content and degree of carbonation, RMC samples with various water content (w/s) of 15%, 20%, and 25% and two different urea content of 3M and 6M were prepared. Water content in this study refers to the amount of bacterial culture. Mixes with 10% of water content were also tried but it was hard to mix. The effect of RMC content was also studied by changing RMC content at 2% of sand weight, varying from 4% to 10%. The 2% of RMC content was too low to form a solid mix in the trial, thus the tests started with a 4% of RMC content. All the mix compositions used in this study are listed in Table 2, and 12 samples were cast for each mix composition under different curing durations at 3, 7, 14, 28 days. In preparation for RMC-based control samples, bacterial culture was replaced by the same amount of water for each mix composition.

Table 2: Mix compositions prepared under this study

Mix	Mix Composition					Curing Conditions
	Sand (g)	RMC (g)	Bacterial Culture (ml)	Water content (w/s)	Urea (g)	
4%MgO	350	14	60	15%	10.8	Air
4%MgO	350	14	80	20%	14.4	Air
4%MgO	350	14	100	25%	18.0	Air
4%MgO	350	14	60	15%	21.6	Air
4%MgO	350	14	80	20%	28.8	Air
4%MgO	350	14	100	25%	36.0	Air
6%MgO	350	21	60	15%	10.8	Air
6%MgO	350	21	80	20%	14.4	Air
6%MgO	350	21	100	25%	18.0	Air
6%MgO	350	21	60	15%	21.6	Air
6%MgO	350	21	80	20%	28.8	Air
6%MgO	350	21	100	25%	36.0	Air
8%MgO	350	28	60	15%	10.8	Air
8%MgO	350	28	80	20%	14.4	Air
8%MgO	350	28	100	25%	18.0	Air
8%MgO	350	28	60	15%	21.6	Air
8%MgO	350	28	80	20%	28.8	Air
8%MgO	350	28	100	25%	36.0	Air
10%MgO	350	35	60	15%	10.8	Air
10%MgO	350	35	80	20%	14.4	Air
10%MgO	350	35	100	25%	18.0	Air
10%MgO	350	35	60	15%	21.6	Air
10%MgO	350	35	80	20%	28.8	Air
10%MgO	350	35	100	25%	36.0	Air

2.3 Unconfined compression strength (UCS) and permeability tests

The unconfined compressive strength of the prepared RMC samples was measured by uniaxial loading in accordance with the specifications of ASTM D2166/D2166M (ASTM). All measurements were performed in triplicates corresponding to three samples from the same batch after 3, 7, 14, and 28 days of curing. The equipment used for this purpose was a Load Frame, operated at a loading rate of 1mm/min. Permeability tests were also conducted on samples after 3, 7, 14 and 28 days of curing through a triaxial cell apparatus followed by the method mentioned by (Carpenter and Stephenson 1986). The initial permeability of pure Ottawa sand only was defined as $5 \pm 2 \times 10^{-3}$ m/s. All measurements were carried out at least three times, unless otherwise specified.

2.4 SEM, TGA and XRD analyses

Representative samples extracted from the columns crashed during UCS test were stored in acetone to stop carbonation process, followed by vacuum drying in preparation for x-ray diffraction (XRD), thermogravimetric analysis/the first derivative of the TGA curve (TGA/DTG) and scanning electron microscopy (SEM) analyses. The dried samples were ground down to pass through a 125 μ m sieve prior to XRD and TGA analyses. XRD analysis was carried out using Bruker Advance D8 equipment and reordered on a Philips PW 1800 spectrometer using Cu K α radiation (40 kV, 40 mA) with a scanning rate of 2 $^\circ$ 2 θ /step from 5 to 80 $^\circ$ 2 θ . Phase quantification was calibrated through the Rietveld refinement software TOPAS 5.0 with a fundamental parameter approach (Cheary and Coelho 1992). The equipment used for TGA/DTG was a Perkin Elmer TGA 4000, performed from 40 to 900 $^\circ$ C with a heating rate of 10 $^\circ$ C /min under nitrogen flow. The SEM analysis was conducted on a Zeiss Evo 50 microscope to evaluate the morphologies of the carbonation products.

3. Results and Discussion

3.1 UCS and permeability

The picture of representative biocarbonated RMC samples is presented in Fig. 2, which were treated with different RMC content but all other conditions kept consistent as 6M of urea and 20% of w/s after early age of 3 days. The first three columns reveal that loose sand after experienced biocarbonation process could form solid sand columns under different RMC content at early age, more details will be discussed later. All control samples were unable to form a firm sand column as the last picture shown. This is because the biocarbonation process could not take place without adding bacterial culture into RMC-based mixes, which is the prerequisite for MICP process.

Figure 2: Biocarbonated RMC samples with different mix compositions

Fig. 3 presents the relationship between 28-day UCS of air-cured biocarbonated RMC samples and water content under different RMC content and urea content. The strength gain demonstrated that the process of biocarbonation and the associated development of a dense HMCs network was generally observed in all RMC samples (Dung and Unluer 2016). It was evident that the UCS of air-cured biocarbonated RMC samples increased with the growth of RMC content from 4% to 8%, but the UCS with 10% of RMC content was slightly lower than the 8% one. This is probably caused by the excessive expansion of RMC at high content of 10%, giving the large expansion expected upon biocarbonation process thus imposing a negative impact on its performance, similar results were also made by (Unluer and Al-Tabbaa 2013, Yi, Liska et al. 2013). Moreover, a higher urea content of 6M was more effective than the lower urea content of 3M. However, for 4% of RMC samples treated by 3M and 6M of urea, the resulting UCS were similar because of insufficient RMC content available in the mixes. Although 6M of urea could generate 0.6M of carbonate via MICP process at 25% of water content, 14 g, as 0.35M of RMC, is inadequate to react with carbonate because one mole of RMC can theoretically react with one mole of carbonate that generated from one mole of urea. With the increase of RMC content to 6% and 8%, the performance of biocarbonation process was improved as more RMC content would involve in biocarbonation during the ongoing curation period. Similarly, mixes with 3M of urea for MICP process could provide insufficient carbonate when 6% of RMC was used, whereas 6% of RMC was inadequate to react with the carbonate produced by 6M of urea. Thus, 8% of RMC samples biocarbonated by 6M of urea to generate carbonate was the optimum mix composition. Subjecting 8% of RMC samples to biocarbonation using 6M of urea at 20% of w/s led to the highest 28-day UCS of up to 2.3 MPa. This indicates that RMC samples can achieve comparable strength with 8% of PC samples when the right mix design and biocarbonation process are provided (Haralambos 2009).

The effect of water content on the strength development of RMC samples can also be observed in Fig. 3. Increasing the w/s from 15% to 20% led to a steady increase in the strength of RMC samples after cured 28 days. A slightly decreasing trend was observed when the w/s was increased from 20% to 25%, leading to a reduction in strength. However, the variance of UCS was

generally less than 10%, thus 20% was considered as optimum w/s in the RMC samples in terms of strength gain and material saving. In the low w/s RMC samples, water was insufficient for both the hydration and carbonation processes. As the water content refers to the bacterial culture used for MICP process, the resulting carbonate is then insufficient for biocarbonation process. The maximum UCS correlated to the 20% of w/s mixes, which given better conditions to facilitate biocarbonation process, thereby leading to higher strength gain. Although 25% of w/s mixes could provide more water for hydration and subsequent biocarbonation, the excessive water present within pore structure would lead to high porosity due to the saturated pore network, thereby resulting in a lower UCS. Overall, the results were in agreement with previous studies, who highlighted the relationship between the w/s, porosity, as well as the developed strength (Kolias and Georgiou 2005).

Figure 3: UCS of 28-day air-cured RMC samples vs. initial water content (w/s)

Fig. 4 shows the effect of curing duration on the strength development of representative RMC samples with different urea content for MICP process at 20% of w/s. Due to the continuous carbonation process, the UCS gradually increased along the curing duration over the entire curing period. A similar trend was observed compared with CO₂ cured soil samples (Yi, Liska et al. 2013, Cai, Liu et al. 2015). A rapid strength increase can be seen at early age, whereby after 3 days the gained UCS ranged from 0.22 to 0.68 MPa. Accordingly, higher RMC and content and higher content of carbonate from MICP process led to a relatively higher early strength. This is mainly because MICP can be completed within a day (Yang, Chu et al. 2019) and the generated carbonate can have a faster diffusion to react with hydrated brucite thus form a certain amount of HMCs to strengthen sand at early age. However, the hydration process of RMC is slow due to their low solubility at room temperature (Shand 2006). As the available unreacted RMC particles remaining

in the matrix slowly hydrated during the curing period and transformed into brucite, the carbonated HMCs formed in the presence of carbonate and contributed to further strength development up to 28 days. Strengths as high as 2.3 MPa was then achieved by enabling the complete carbonation via the optimization of the use of RMC under optimum w/s and MICP process (Ruan and Unluer 2017). The strength is as good as those samples required several repeated treatments via the conventional MICP method (Cheng, Shahin et al. 2019).

Figure 4: UCS of RMC samples at different curing durations

Apart from the strength gain of biocarbonated RMC samples, the permeability was also significantly decreased as the produced HMCs served as pore materials to reduce pore volumes within the sand matrix. Unlike conventional measurement of water sorptivity or weight increment that reflects carbonation ability, permeability tests of biocarbonated RMC samples were used to provide a direct approach of measurement of capillary pores. The permeability of all RMC samples cured for up to 28 days is shown in Fig. 4. It was observed that all RMC-based samples experienced a significant permeability reduction after biocarbonation process. According to Fig. 5, further permeability reduction was achieved by the increase of water content from 15% to 25% under the same urea content and w/s in the RMC-based mixes. This was because the increase of w/s led to a higher amount of brucite accompanied with a lower residual RMC content, as expected. Although the formation of brucite has little influence on strength development, it could also enable the reduction of pore volumes and lower permeability. In addition, changing the urea content from 3M to 6M used for MICP process also facilitated the reduction of permeability in the RMC-based mixes. This was attributed to the MICP process with higher urea content that could generate more carbonates for hydrate and carbonate reactions during the continuous biocarbonation process. These reactions led to the formation of RMCs associated with the reduction of porosity via the

expansive nature of biocarbonation process, whose formation led to the filling up of pore space among sand particles (Ruan and Unluer 2017). Therefore, the lowest permeability is generally consistent with the use of RMC content and urea content as well as w/s in the RMC samples. The results in this study suggest that higher RMC content with higher urea content at higher w/s can result in the lowest permeability via the cooperation of hydration and the carbonation process as well as their resulting products. Although the permeability of 10% RMC sample with 6M of urea content at 25% of w/s was lowest at 8.8×10^{-8} m/s after 28 days of curing, it must be noted that the variance of permeability between 8% RMC sample with 6M of urea content at 20% of w/s under same curing duration was less than 5%, however, the latter mix composition performed highest UCS. On the other hand, 10% RMC samples might cause excessive expansive and bring a negative effect on permeability reduction as well as other performances. For example, excessive expansion may cause microcrack within dense HMCs network structure, leading to poor performance on permeability reduction and strength development. Thus, the 8% RMC sample with 6M of urea content at 20% of w/s was taken as representative mix composition. Subjecting the representative RMC samples to biocarbonation up to 28 days led to a permeability reduction to 1.8×10^{-7} m/s from the initial level of 10^{-3} m/s, which was also comparable with that achieved by well-compacted clay (Daniel and Wu 1993). Compared to the conventional CO_2 cured RMC samples, the porosity and water sorptivity undergo a significant reduction after carbonation due to the formation of the dense layer, that is, HMCs, which is consistent with the results in this study (Ruan and Unluer 2017).

Figure 5: Permeability of 28-day air-cured RMC samples vs. initial water content (w/s)

Fig. 6 displays the effect of curing duration on the permeability reduction of all RMC samples with different urea content for MICP process at 20% of w/s. It can be seen that longer

curing duration led to a constant decrease in the permeability of RMC samples. This was associated with the formation of carbonate phases over the entire curing period, constantly filling out the pores and finally forming a densified structure to reduce the overall permeability. The representative sample, reported as above, had a low permeability to the 7.3×10^{-6} m/s at early curing age of 3 days, it demonstrated a relatively higher hydration degree and some extent of carbonation degree, contributing to the permeability reduction. It is notable that the permeability reduction at early age was significant in RMC samples for engineering practice in terms of efficient soil improvement. Afterward, the permeability was reduced to 1.5×10^{-6} m/s after 7 days of curing and which could drop further to 1.8×10^{-7} m/s up to 28 days due to subsequent biocarbonation process. This would be hardly feasible using the conventional MICP methods as reported before (Yang, Chu et al. 2019). Therefore, the proposed biocarbonation method of RMC samples is a more efficient method than the conventional MICP method not only in terms of strength development but also in permeability reduction.

Figure 6: Permeability of RMC samples at different curing durations

3.2 XRD

Fig. 7 depicts the XRD pattern of biocarbonated samples using 8% of RMC with 6M of urea at 20% of w/s after 28 days of curing. Among some peaks of other phases, the representative carbonate phases observed was hydromagnesite as well as a minor formation of nesquehonite, at relatively high peaks of 15.3° and 30.3° 2θ , respectively. In addition to the HMCs, the representative sample also revealed the presence of brucite, unreacted MgO (periclase) and SiO_2 (Quartz). Brucite is from hydration process but remains unreacted for the carbonation process, while SiO_2 is usually peeling from Ottawa sand.

Figure 6: XRD pattern of 8% RMC sample with 6M of urea and 20% of w/s after 28 days of curing (P: Periclase; B: Brucite; H: Hydromagnesite; N: Nesquehonite; Q: Quartz)

Table 3 lists quantities of major phases within samples extracted from 28 days cured sand columns mixed with 6M of urea at 20% of w/s. Then, the correlation between the HMCs contents and developed UCS is plotted and presented in Fig. 8. All samples presented a low content of unreacted MgO, showing a high utilization rate of RMC in the hydration and subsequent carbonation process. By changing RMC content from 4% to 8%, the results indicated that the higher total amount of hydromagnesite and nesquehonite contents cooperatively contributed to higher strength development from 0.83 to 2.3 MPa, whereas the lower UCS sample composed of relatively high content of brucite rather than HMCs. This was probably because lower RMC content of 4% could experience a higher conversion of MgO into brucite under the same w/s, however, it might be less effective on carbonation because of insufficient RMC content. These results suggest that higher strength can be achieved via the optimization of complete carbonation, which has been discussed earlier. When compared to 8% and 10% RMC samples revealed that the total amount of hydromagnesite and nesquehonite contents were similar but different strengths. Considering its relatively higher content of hydromagnesite of 8% RMC samples than the 10% one, it in turn highlights that the strength development not only relies on the amount of HMCs, but also on the morphology of them. This was consistent with the previous findings (De Silva, Bucea et al. 2009). By contrast, RMC samples with higher hydromagnesite content demonstrated higher strength compared to the sample with higher Nesquehonite content, this could be explained by that the hardness of Hydromagnesite is 3.5, higher than the Nesquehonite with a hardness of 2.5 (Harrison and FCPA 2005). Another factor to consider is the increased RMC content within the samples, which would lead to a higher pH value during hydration. However, a higher pH value is detrimental to bacteria cells (Yang, Chu et al. 2020), resulting in a poor carbonation performance as bacteria have played a significant role in generating carbonate for this proposed biocarbonation

process, which is also reflected by the slightly lower amount of HMCs presented in 10% RMC-based mixtures compared with 8% RMC-based mixtures.

Table 3: Quantification of major phases within samples mixed with 6M of urea at 20% of w/s, after 28 days of curing

Mixture		Percentage (%)				
RMC	Periclase	Brucite	Quartz	Hydromagnesite	Nesquehonite	HMCs*
4%	5.9	32.3	0.5	58.3	3.0	61.3
6%	4.6	16.8	0	30.9	47.7	78.6
8%	1.9	5.2	0.1	72.6	20.2	92.8
10%	2.8	5.9	0.4	14.6	76.3	90.9

*: The amount of hydromagnesite and nesquehonite

Figure 7: The correlation between the HMC contents and UCS

3.3 TGA

Fig. 9 shows the TGA/DTG curves of biocarbonated RMC samples with 6M of urea at 20% of w/s after 28 days of curing. There are three major decomposition processes in line with previously published results (Frost, Bahfenne et al. 2008, Vágvolgyi, Frost et al. 2008, Ballirano, De Vito et al. 2010, Hollingbery and Hull 2010, Frost and Palmer 2011, Jauffret, Morrison et al. 2015, Purwajanti, Zhou et al. 2015), as follow:

- (1) 80 to 280 °C: Dehydration of water bonded to HMCs,

$4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O} \rightarrow 4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 + 4\text{H}_2\text{O}$ (Vágvölgyi, Frost et al. 2008, Ballirano, De Vito et al. 2010, Frost and Palmer 2011, Jauffret, Morrison et al. 2015, Purwajanti, Zhou et al. 2015)

(2) 280 to 500 °C: Dehydroxylation of HMCs,

$4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \rightarrow 4\text{MgCO}_3 + \text{MgO} + \text{H}_2\text{O}$ (Ballirano, De Vito et al. 2010, Hollingbery and Hull 2010, Frost and Palmer 2011, Jauffret, Morrison et al. 2015)

Decarbonation of nesquehonite,

$\text{MgCO}_3 \cdot 3\text{H}_2\text{O} \rightarrow \text{MgO} + \text{CO}_2 + 3\text{H}_2\text{O}$, and

Decomposition of unreacted brucite,

$\text{Mg}(\text{OH})_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$

(3) 500 to 900 °C: Decarboantion of HMCs,

$\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$ (Frost and Palmer 2011, Jauffret, Morrison et al. 2015)

Figure 9: TGA/DTG curves of RMC samples with 6M of urea at 20% of w/s after 28 days of curing

The weight losses of RMC samples with 6M of urea at 20% of w/s after 28 days of curing under each reaction taken place are listed in Table 4 in line with the temperature ranges listed above, accompanying with the corresponding H₂O and CO₂ contents. The loss of water associated with brucite decomposition was differentiated from the dihydroxylation of HMCs that took within the same temperature range via the data presented earlier in Table 3. The total weight loss increased with the RMC content, which was associated with a higher HMC content. In line with the XRD quantification results, biocarbonated sample with 8% of RMC content and 6M of urea content at 20% of w/s showed a highest CO₂ loss corresponding to the highest HMC content and UCS than

others, indicating a direct relationship between the extent of carbonation and mechanical performance. Despite the similar amount of HMC content between 8% and 10% RMC samples, variations of their developed strength highlighted the importance of the morphology of the carbonate phases, rather than their content, in strength development. This was consistent with earlier explanations.

Table 4: Weight loss observed in RMC samples with 6M of urea at 20% of w/s, after 28 days of curing

Mix	Weight loss (wt.%)					Total
	80 - 280 °C	280 - 500 °C	500 - 900 °C	H ₂ O (Decomposition of brucite)	CO ₂ (Decomposition of HMCs)	
4%,6M,20%	15.6	29.4	9.3	10.0	28.0	54.3
6%,6M,20%	21.5	28.5	8.3	5.2	31.8	58.3
8%,6M,20%	25.3	32.2	8.1	1.6	38.4	65.6
10%,6M,20%	27.1	31.4	8.1	1.8	37.2	66.6

3.4 SEM

The microstructures of biocarbonated RMC samples were examined using SEM. Fig. 7 presents the SEM images of best performing 8% RMC sample biocarbonated by 6M of urea with 20% of w/s that cured for 28 days. Fig. (10a)-(10i) shown that sand particles were surrounded by HMCs, connecting the loose sand particles and filling out the pores among the sand. The interconnected and well-developed HMC crystals have an effective binding ability that can form a strong network structure and then lead to strength development. In addition to strength gain, the expansive formation of HMCs via the reaction between brucite and carbonate can reduce the porosity and associated with the densification of microstructure, resulting in a dramatic reduction of permeability (Ruan and Unluer 2017). This was evident by the UCS and permeability result of RMC samples after 28 days of biocarbonation discussed earlier.

As reported by previous XRD and TGA results, the HMCs extracted from biocarbonated RMC samples consisted of hydromagnesite and accompanied by nesquehonite. The main carbonate phases observed in representative samples were typical hydromagnesite (d)-(f) and nesquehonite (g)-(i) crystals, in line with XRD results. The products of typical hydromagnesite and nesquehonite were identified by its rosette-like structure and needle-like structure, respectively. The dense and closely packed formation of hydromagnesite, accompanying with fewer nesquehonite could explain the contribution of higher strength. Previous results have demonstrated that hydromagnesite and nesquehonite are the dominated crystals during the carbonation process and attributed to most of the strength development (Ruan and Unluer 2017). In line with XRD and TGA results, 8% RMC sample biocarbonated by 6M of urea with 20% of w/s that cured for 28 days revealed the highest HMCs content (hydromagnesite and nesquehonite) corresponding to highest strength. Although 10% RMC sample with the same mix composition and curing conditions indicated a similar amount of HMCs, the expansion and pH issue of using higher RMC content may also take into consideration for strength development as reported earlier.

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

Figure 10: SEM images of 8% RMC sample biocarbonated by 6M of urea with 20% of w/s, after 28 days of curing: (a)-(c) biocarbonated RMC sample; (d)-(f) microstructure of hydromagnesite; (g)-(i) microstructure of nesquehonite

4 Conclusions

This study presented a novel approach for soil improvement using microbially induced carbonate precipitation (MICP) technique to carbonate RMC, which enabled the bridging of sand particles together. The detailed microstructural investigation of the prepared samples confirmed the formation of two commonly observed HMCs in RMC systems, hydromagnesite and nesquehonite, as the main carbonation products. The rosette-like hydromagnesite and needle-like nesquehonite cooperatively contributed to the formation of a dense HMC network, enabling the binding of particles within the biocarbonated RMC samples. Increasing the RMC concentration from 8% to 10% had an adverse effect on mechanical performance, albeit the comparable HMC contents. This decline in strength was attributed to the expansive nature of RMC and the influence of pH on the MICP process. A direct correlation between the hydromagnesite content and strength was observed. Hydromagnesite had a great influence on mechanical performance than

nesquehonite, which could be associated with the higher hardness of the former. Therefore, the obtained results highlighted the importance of the morphology of the formed carbonates rather than their quantity on the performance of biocarbonated samples.

Out of the formulations investigated in this study, the combination of 8% RMC with 6M urea at a w/s of 20 was identified as the optimum condition for the biocarbonation of RMC samples. This combination led to improved performance, resulting in a strength of ~2.3 MPa at 28 days, along with a low permeability at $\sim XX \times 10^{-7}$ m/s. More importantly, the biocarbonation process facilitated strength development and permeability reduction at early ages due to the rapid formation of carbonate phases via MICP. The performance of RMC-based samples was comparable with corresponding PC-based samples, highlighting the feasibility of the proposed biocarbonation approach to be used for soil improvement on a larger scale.

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