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Impact of hydrated magnesium carbonate additives on the carbonation of reactive MgO cements

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Abstract:

Reactive magnesia (MgO) cements have emerged as a potentially more sustainable and technically superior alternative to Portland cement due to their lower production temperature and ability to sequester significant quantities of CO₂. Porous blocks containing MgO were found to achieve higher strength values than PC blocks. A number of variables are investigated to achieve maximum carbonation and associated high strengths. This paper focuses on the impact of four different hydrated magnesium carbonates (HMCs) as cement replacements of either 20 or 50%. Accelerated carbonation (20°C, 70-90% RH, 20% CO₂) is compared with natural curing (20°C, 60-70% RH, ambient CO₂). SEM, TG/DTA, XRD, and HCl acid digestion are utilized to provide a thorough understanding of the performance of MgO-cement porous blocks. The presence of HMCs resulted in the formation of larger size carbonation products with a different morphology than those in the control mix, leading to significantly enhanced carbonation and strength.

Keywords: (B) Microstructure; (B) Thermal analysis; (C) Carbonation; (C) Compressive Strength; (D) MgO

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1. Introduction

Concrete made from Portland cement (PC), with a global production of over 3 billion tonnes per year [1], is the most widely used building material in the world. Although significant advances have been made in durability and strength aspects, there are still major issues associated with the environmental impacts of the production process. A significant quantity of CO₂, ~0.85 t/t, is emitted during the calcination process of limestone at ~1450°C, from the combustion of fuels in the kiln, as well as from power generation. Accordingly, the cement industry contributes to 5-8% of global anthropogenic CO₂ emissions [2, 3], making it a critical sector for CO₂-emission mitigation strategies. Three global initiatives are currently being practiced: (i) partial cement replacements with low carbon materials, industrial by-products and wastes, (ii) improvement of overall energy efficiency with the use of alternative raw materials, renewable energy sources, and low-energy production methods, and (iii) development of new cement formulations with lower energy consumption and carbon footprints; an example of which is the recently developed reactive magnesia (MgO) cements.

MgO cements [4] are a mixture of PC and reactive magnesia in different proportions, depending on their intended application. The sustainability advantages of MgO over PC include: (i) ability to sequester significant quantities of CO₂, (ii) considerable durability enhancement due to the higher resistance of the hydration and carbonation products in aggressive environments where reinforcement is not present, (iii) lower sensitivity to impurities enabling the utilization of large quantities of waste and industrial by-products and (iv) potential to be fully recycled where MgO is used alone as the binder, as its carbonation process produces magnesium carbonates, which are the predominant source for the production of magnesia. Alternatively, certain limitations exist regarding the manufacture and implementation of MgO cements in the construction sector. These include the unfamiliarity, insufficient documentation and low record of reliability of MgO as opposed to the high validation and market confidence of PC; and the relatively low availability of the raw materials and

proximity to existing production facilities, a majority of which is located in China, leading to increased environmental impacts.

Magnesia can be categorized under three main grades: Reactive MgO is produced at around 700-1000°C and has the highest reactivity and surface area, whereas hard-burned and dead-burned MgO are calcined at higher temperatures of 1000-1400°C and 1400-2000°C, respectively, and have correspondingly lower reactivity and surface areas. Unlike dead-burned MgO, whose use in clinkers is disadvantageous due to its slow hydration rate resulting in large and localized volume increases that can cause expansion and cracking in the hardened cement product, reactive MgO hydrates at a similar rate to PC, thereby eliminating these problems [5].

Extensive research has been conducted at the University of Cambridge since 2004 into the fundamental properties of reactive MgO alone as well as PC-MgO blends including hydration behaviour [5-8], microstructure [7], and carbonation performance [9-13]. The use of MgO alone was observed to have special advantages in terms of mechanical and durability performance and CO₂ sequestration potential over the PC-MgO blends depending on the application [10, 11, 14, 15], leading to successful commercial scale-up trials [12, 13]. This work showed that porous blocks containing 10% MgO for their cement component achieved compressive strengths more than twice of the corresponding PC blocks under elevated CO₂ curing, where the strength development was related to the degree of carbonation. Other applications included MgO as an additive in PC and GGBS-based concretes [16], in PC and fly ash blends used in contaminant immobilisation [17, 18] and with GGBS and/or PC and/or pfa in blends prepared for soil stabilization [16, 19], with very promising results.

The above work has shown that in porous blocks where reactive MgO is used alone as the cement component, MgO hydrates to form brucite (Mg(OH)₂, magnesium hydroxide), which is quite weak. However, when subjected to the right curing conditions, brucite can then react with CO₂ and additional water as appropriate, to form a range of strength providing hydrated magnesium carbonates (HMCs),

mainly nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), hydromagnesite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), and dypingite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$). The dense formation of nesquehonite, as observed in previous studies [20, 21] produces higher strengths than similar mixes where dypingite/hydromagnesite is the main component forming after the carbonation process. Carbonation of MgO into nesquehonite, which has an elongated needle-like morphology, involves a significant volume expansion during which the solid volume is increased by a factor of 2.34 upon its conversion from brucite [22], reducing porosity and hence increasing stiffness. This could also be explained by the growth of fibrous and acicular crystals of nesquehonite, the main contributor to the microstructural strength, especially advantageous when compared to other carbonates with rounded or tabular crystals [23], independent of the particle size [24].

Nesquehonite is a low-temperature carbonate normally found in alkaline soils, cave deposits and as a weathering product of ultrafamic rocks. One problem with its formation is its instability at temperatures above 50°C , making it unsuitable for some applications involving high temperatures. In such cases, nesquehonite transforms into thermodynamically more stable HMCs, such as dypingite or hydromagnesite [25-27], which have a $\text{CO}_2\text{:Mg}$ ratio lower than that of nesquehonite. Although these more stable carbonates can still provide high strengths, transformation of nesquehonite into these HMCs could lead to a reduction in mechanical strength due to the associated structural changes. In addition to CO_2 concentration and temperature, other parameters including water activity or pH also influence the formation of different HMCs. When subjected to thermal analysis, HMCs decompose by a series of endothermic reactions and result in the emission of H_2O and CO_2 . Several studies [28-31] have investigated the thermal decomposition steps of hydromagnesite and dypingite. Accordingly, the thermal decomposition of hydromagnesite proceeds via dehydration at $100\text{--}300^\circ\text{C}$ and decarbonation at $350\text{--}650^\circ\text{C}$ toward the end product, MgO. Overall, the transformation pathway of HMCs follows the trend below:

In porous blocks, the rate and degree of carbonation, the formation of HMCs, and the associated strength development depend on several contributing factors including composition and characteristics of MgO, block mix design, use of additives and admixtures, particle size distribution of the aggregates, particle packing, and porosity of the hardened concrete as well as curing conditions (namely relative humidity, temperature, transport and partial pressure of CO₂) [14, 32-36]. Only a small number of these variables have been considered in the previous work reported above. The work reported in this paper, which is part of an extensive investigation into the effect of these variables, concentrates on the impact of HMCs as part of the cement component in carbonated MgO porous blocks.

The aim of this work is to achieve up to 100% carbonation via the inclusion of a range of HMCs as a part of the cement component. Addition of HMCs within the initial mix design can reduce the formation of brucite film on the MgO surface, therefore increasing the surface area exposed to carbonation and enabling the continuous hydration of MgO. This alteration of the hydration mechanism can provide space for the formation of carbonate products, which will enhance the carbonation process and lead to higher strength results. Carbonation rate of brucite crystals produced during hydration can also increase because the addition of HMCs can act as seed crystals and provide nucleation sites for accelerated carbonate formation [14, 37, 38]. Hence the objectives of this work are to:

- (a) Investigate the influence of a range of HMCs as a part of the cement component on the carbonation of porous blocks
- (b) Provide a comparison of blocks cured under accelerated and natural CO₂ conditions in terms of strength, degree of carbonation, and microstructural development
- (c) Examine the effect of different water contents in enhancing the degree of carbonation and subsequently strength for each mix
- (d) Quantify the degree of carbonation of blocks with different compositions by using several methods (i.e. TGA, XRD, and dissolving in HCl acid)

2. Materials and methods

The reactive magnesia used was grade 94/325 obtained from Richard Baker Harrison, UK. Four different high purity commercial HMCs obtained from different sources (Fisher Scientific and Acros Organics) and characterized as “light” (LHMCs) and “heavy” (HHMCs) were included within the mixes. Defined with the general formula, $x\text{MgCO}_3 \cdot y\text{Mg}(\text{OH})_2 \cdot z\text{H}_2\text{O}$, where $y=1$, light (LHMC), with the empirical formula $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, corresponds to hydromagnesite; and heavy (HHMC), with the empirical formula $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, corresponds to dypingite [28]. The light form is 2-2.5 times more bulky than the heavy. A detailed study into the characterization of these HMCs using microstructure and thermal analysis was presented in a recent study [39]. In terms of cement content, the MgO or MgO-HMC blends (in ratios of 1:1 or 4:1) was always 10% of the dry mix. Pulverized fuel ash (pfa), obtained from Ratcliffe-on-Soar power station in Nottingham, UK, was used as a filler in the blocks and made up 5% of the dry material. The chemical composition of the MgO and pfa are presented in Table 1. Natural aggregates consisting of sharp sand (0-4mm, with $D_{50}=0.7\text{mm}$, $C_U=3.6$) at 50% content, and gravel (2-10mm, with $D_{50}=6.5\text{mm}$, $C_U=1.75$) at 35% content were used together with the 5% pfa to form the 90% content aggregate mix, as used in previous related work [20, 21].

The dry powders of MgO, HMCs, pfa and aggregates were initially mixed together in a bench-scale food mixer, after which a previously determined amount of water was added. Mixes involving HMCs contained 85% natural aggregates, 5% pfa, and 10% cement by mass, which was composed of MgO:HMCs at a ratio of 1:1 or 4:1. The starting point control mix was that used in a previous related study [20], where the cement content was composed of 10% MgO alone and the water content was also optimized at a w/c ratio of 0.8. All the different mix compositions tested are listed in Table 2. The chosen w/c ratios were related to the standard consistence (SC) of the individual mixes.

Table 1

Chemical composition and physical properties of the MgO and pfa used, based on supplier datasheets (NM = not measured)

	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	Specific gravity	D ₅₀ (μm)	Specific Surface area (m ² /g)	Loss on ignition (%)
MgO	2.0	1.0	NM	NM	>94.0	3.00	45.0	16.3	2.0
Pfa	6.8	49.3	9.7	24.1	1.1	2.26	12.0	2.6	3.9

Equal weights of mix were placed in metal cylindrical moulds, 50mm in diameter and the samples were then produced in a laboratory uni-axial press by applying a force of 5 kN. The produced samples, 65-75mm high, were then immediately de-moulded and placed in the relevant curing environments. Two main curing conditions were used: natural curing (20°C, 60-70% relative humidity (RH), and ambient CO₂) for 28 days, and accelerated carbonation curing (20°C, 70-90% RH and 20% CO₂ concentration) in an environmental incubator for 7 days.

Table 2

Composition of the mixes produced

HMCs Type	Mix no.	Cement (%)		Water/cement ratio (Optimum w/c in bold)
		MgO	HMC	
Control	C	10	0	0.80
HHMC	HHMC-50	5	5	0.84, 0.89 , 0.95, 1.01
	HHMC-20	8	2	0.75, 0.81 , 0.85, 0.92
LHMC1	LHMC1-50	5	5	1.20, 1.24 , 1.28, 1.33, 1.44
	LHMC1-20	8	2	0.83, 0.88, 0.92 , 0.97, 1.02
LHMC2	LHMC2-50	5	5	1.07, 1.17 , 1.25, 1.33
	LHMC2-20	8	2	0.82, 0.88 , 0.94, 1.02
LHMC3	LHMC3-50	5	5	0.83, 0.86, 0.90, 0.94 , 0.98

The SC of all the materials used in this study were measured according to BS EN 196-3:1995 [40]. Accordingly, SCs of MgO and pfa were 0.6 and 0.4, respectively. Among the HMCs, HHMC had a SC of 0.7, as opposed to 2.64, 2.28 and 1.1 for LHMC1, LHMC2, and LHMC3, respectively. The calculation of porosity involved measuring and subtracting the sample mass after drying at 70°C from the saturated mass and dividing the result by the overall volume. The unconfined compressive strength (UCS) was measured by uni-axial loading of the samples in triplicates. The microstructure of representative samples from outer surface of the samples was observed by imaging fracture surfaces in a scanning electron microscope (SEM), JEOL JSM-5800 LV, facilitating elemental composition analysis. Before the SEM analysis, samples were broken into smaller pieces and then vacuum dried for a few days to make sure all the moisture was removed. Once ready, small pieces from each mix were placed on metal stubs by using carbon paste, dried for 10-20 minutes, and were sputter coated with gold before being placed into the microscope.

Three different methods were used for the quantification of carbonation: Thermogravimetry/differential thermal analysis (TG/DTA), X-ray diffraction (XRD), and acid digestion. X-ray diffraction (XRD) was utilized to provide qualitative and quantitative analyses of the crystalline phases present within the mixes. XRD analysis was conducted on a Siemens D500 Diffractometer. The samples were broken down to small pieces (e.g. <5mm) and then quartered before being ground down to 125µm to be analyzed under XRD. The relative diffraction peaks of various carbonates, $\text{Mg}(\text{OH})_2$ and MgCO_3 in each mix were identified by using X-ray diffraction analysis under the operating conditions of Cu K α radiation (40 kV, 40 mA); scan rate: 2°/step; 2 θ : 5-50°. The RIR technique [41-45] was applied for the quantitative analysis of the phases present by making use of a standard phase with a known proportion, whose integrated intensity is compared to that of the phase of interest. The internal standard used for quantification purposes was fluorite (CaF_2) at 20 wt% [46]. Calibration curves for magnesia and brucite, which were the components used for quantitative analysis, were straight lines through the origin i.e. $y=kx$, where x is the RIR of the phase analyzed and y is the weight fraction of the component investigated. The value of k was 0.2886 for magnesia and 0.3651 for brucite [11]. The

RIR was acquired through dividing the integrated intensity of the strongest line of the phase with that of the standard.

The thermogravimetric analysis instrument used was a Perkin Elmer STA 6000, controlled by Pyris software. Initially the sample powder was obtained using a 75 μ m sieve. To start the analysis, the powder was placed in a crucible designed for use with the TGA instrument, where the samples were heated in air from 40°C to 1000°C at a rate of 10°C/minute. The change in mass with the increasing temperature was recorded to provide qualitative and quantitative information. Another method to measure the amount of CO₂ absorbed during carbonation was by acid digestion using hydrochloric (HCl) acid. This process involved neutralizing of solutions containing CO₂ decomposed chemically by HCl acid.

3. Results and discussion

3.1 Strength development and porosity

The strength results for each of the four HMC containing mixes subjected to accelerated carbonation over a range of water contents are indicated in Fig. 1. It is clear that for all four mixes there was an optimum w/c ratio which produced the highest strength value. Given that the highest strength obtained by the control mix, which only included MgO with no HMCs, was 18 MPa, the only mix containing HMCs that outperformed the control mix was HHMC-20 (Fig. 1(a)), achieving a strength of 22MPa. The dense microstructure of the HHMC, along with its low water demand (SC of 0.7 as opposed to 2.64, 2.28 and 1.1 for LHMC1, LHMC2, and LHMC3, respectively) and high CO₂ content determined earlier in a previous study [39], can explain its superior performance. The SC of the HHMC is only slightly higher than that of MgO at 0.6, presenting an advantage over the LHMCs in terms of regulating the overall water demand of the mixes it was included in. The three LHMCs all

produced similar maximum strength values of around 15-17MPa. Within each mix composition, higher values were produced by those where the MgO:HMC ratio was 4:1. Mixes with 1:1 ratio produced lower strengths of 14MPa for the HHMC, again higher than those with LHMCs, and 8-10MPa for the LHMCs, as expected. The higher strength results achieved by the 4:1 mixes were mainly attributed to the higher MgO content, presenting the potential for carbonation.

The best performing mixes out of each composition were tested for porosity before and after accelerated carbonation of 7 days. The measured porosity values before and after carbonation ranged between 15.8-17.1% and 14.9-16.3%, respectively. Mix HHMC-20 indicated the highest decrease in porosity by 7.5%, followed by LHMC3-20, LHMC2-20, LHMC1-20, and HHMC-50, whose porosities decreased by 4.4-4.7% after carbonation. In general, a higher change in porosities were observed for mixes where the MgO:HMC ratio was 4:1 when compared to the corresponding mixes where this ratio was 1:1. Since the decrease of porosity after carbonation is linked with the amount of CO₂ sequestered and hence the formation of strength providing carbonation products, the porosity results were directly correlated with the strength measurements.

Fig. 2 presents the corresponding results for the naturally cured mixes. In this case, the control mix, containing only MgO, produced the highest strength, whereas mixes containing HMCs led to quite low strength values. These results show that the addition of HMCs in naturally cured mixes offers no benefits and in fact has detrimental effect on the strength of the block samples. This could potentially be due to the lack of sufficient CO₂ and its low diffusion, discussed further in Section 3.2, within mixes with higher water contents in accordance with the high SC of the HMCs used, resulting in limited carbonation and hence lower strengths. It is possible that a different behavior could arise for longer periods of natural curing than the 28 days used in this study. This requires further investigation, especially for the HHMC mix that outperformed the control mix during accelerated carbonation.

(a)

(b)

(c)

(d)

Fig. 1. UCS of the four HMC mixes with two MgO:HMC ratios and different water/cement ratios after 7 days of accelerated carbonation

Fig. 2. UCS of the naturally cured samples after 28 days

3.2 Microstructure

Figs. 3-5 show the SEM images of all the mixes after the 7 day accelerated carbonation curing period. Fig. 3(a) of the control mix shows abundance of mainly dypingite/hydromagnesite. The slight presence of MgO could also be seen amongst the dypingite/hydromagnesite indicating that hydration of MgO was not complete in the control mix. The images of all the mixes containing HMCs suggested abundance of hydromagnesite/dypingite and nesquehonite. Mixes including HHMC as a part of their cement component, shown in Figs. 4(a) and (b), indicated the formation of different HMCs, depending on the ratio of MgO and HHMC within the mixes. For those mixes with an MgO:HMC ratio of 1:1, widely spread dypingite/hydromagnesite was observed, whereas nesquehonite was the main resulting carbonation product when this ratio was 4:1. The fact that different HMCs can form when the initial HMC content varies within a mix can also explain the discrepancy within the strength results. The presence of a dense layer of nesquehonite in the case of mix HHMC-20 was the main reason for the significant strength development, whereas uncarbonated brucite was observed for some of the mixes

containing LHMCs at a ratio of 1:1 with MgO, indicating that carbonation had not fully taken place at the end of the curing period and hence the lower strength results.

Although the control and HHMC-50 mixes both produced HMCs resembling dypingite/hydromagnesite, they differed in shape and size. Those present in the control mix, shown in Fig. 3(a), were smaller and more round, while each particle of dypingite/hydromagnesite of the HHMC-50 mix, shown in Fig. 4(a) had a more rosette-like morphology and was at least 3 times larger. On the other hand, the formation of nesquehonite as opposed to dypingite/hydromagnesite was observed in mix HHMC-20 with the lower initial HMC content. In LHM1-50 mix, a vast amount of brucite was observed (Fig. 4(c)), indicating lack of carbonation, also explaining the low strength results obtained. Alternatively, carbonation of LHM1-20 mix led to the formation of dypingite/hydromagnesite (Fig. 4(d)), also reflected by the different strength results. While a widely spread network of dypingite/ hydromagnesite was seen in mixes LHM2-50 and LHM2-20 (Figs. 5(a) and (b)), the former mix resulted in larger and flakier particles whereas smaller particles were dominant within the latter. A similar trend was followed by mixes LHM3, shown by Figs. 5(c) and (d). However, the much more closely knitted structure of dypingite/hydromagnesite forming as a result of the carbonation of mix LHM3-20 was also justified by the relatively higher strength results obtained by these mixes.

In general, amongst the mixes where dypingite/hydromagnesite was the main carbonation product, it was seen that as the initial HMC content increased, the overall size of dypingite/hydromagnesite particles forming as a result of the carbonation process increased, along with a difference in morphology. These mixes with the larger sized dypingite/hydromagnesite also resulted in lower strengths than corresponding mixes with lower HMCs contents, whereas the development of nesquehonite resulted in significantly higher strength results, as opposed to all the other mixes where dypingite/hydromagnesite was the main carbonation product.

(a)

(b)

Fig. 3. SEM images of control mix cured under (a) accelerated carbonation, (b) natural curing

(a)

(b)

(c)

(d)

Fig. 4. SEM images of mixes cured under accelerated carbonation (a) HHMC-50, (b) HHMC-20, (c) LHMC1-50, (d) LHMC1-20

Fig. 5. SEM images of mixes cured under accelerated carbonation (a) LHMC2-50, (b) LHMC2-20, (c) LHMC3-50, (d) LHMC3-20

The SEMs of samples subjected to natural curing, shown in Figs. 6(a) to (i), demonstrated relatively uncarbonated microstructures where some brucite was present in small quantities. Although the formation of dypingite/hydromagnesite was seen in some mixes, the lack of carbonation was highlighted by the presence of uncarbonated MgO and brucite particles spread around the microstructure in general, explaining the low strength results (i.e. <4MPa) generated by the naturally cured samples. However, it should be noted that due to the low CO₂ concentration in air (~0.039%), natural curing takes place at a much slower rate than accelerated carbonation where the CO₂ concentration was 20% and 28 days is a considerably short period of time for carbonation to take place under natural conditions. To maintain a certain level of humidity during such periods of carbonation and prevent the drying out of samples, water was sprayed on them at regular intervals,

which introduced the possibility of available pores within the samples getting blocked by additional water molecules. Considering that the diffusion coefficient of CO_2 is $16 \text{ mm}^2/\text{s}$ in air and $0.0016 \text{ mm}^2/\text{s}$ in water (i.e. CO_2 diffuses 10,000 faster in air than in water) [47], the transport of CO_2 through water molecules occupying the pores of porous blocks would be much harder, thereby slowing down carbonation. On the other hand, as seen previously, much longer periods of natural curing would minimize these effects and lead to a more extensive formation of HMCs [21].

Fig. 6. SEM images of mixes cured under natural conditions (a) control mix, (b) HHMC-50, (c) HHMC-20, (d) LHMC1-50, (e) LHMC1-20, (f) LHMC2-50, (g) LHMC2-20, (h) LHMC3-50, (i) LHMC3-20

3.3 X-Ray diffraction

Only the samples subjected to accelerated carbonation were tested using XRD and TGA. Fig. 7 shows the x-ray diffractograms of all mixes after 7 days of accelerated carbonation. The peak of fluorite (F) located at 28.25° 2Theta was used as an internal standard for the quantification of CO_2 sequestration. All the mixes showed the presence of quartz from the aggregates. In those mixes where hydration was not completed up to a 100%, the presence of MgO was observed. For all mixes but the control mix and LHMC1-50, there was no brucite peak, meaning that all the brucite initially formed from the hydration of MgO had been fully consumed during carbonation, which was also obvious from SEM images. In terms of HMCs forming as a result of carbonation, small peaks of nesquehonite, dypingite, and hydromagnesite were present in all mixes, even though the SEM images only revealed the formation of only one of these HMCs for each mix. While the small sample chosen for SEM analysis may not be entirely representative of the whole mix and show all the products of carbonation, these HMCs have several overlapping peaks, presenting a challenge in identifying each one of them separately by XRD analysis.

3.4 Thermal analysis

The TG/DTA curves of all mixes are presented on Fig. 8. The relatively small weight loss at $<100^\circ\text{C}$ was due to the loss of hygroscopic water. The control mix illustrated two distinct endothermic peaks. The first peak at 411°C refers to the removal of water of crystallization within the HMC formed as a result of carbonation and the decomposition of brucite into MgO; whereas the second peak at 748°C refers to the decarbonation of the magnesite into MgO. The reaction involving the decomposition of brucite was due to the (i) brucite which formed as a result of the hydration of MgO but was left uncarbonated and (ii) brucite due to the dehydroxylation of the HMC.

Seven different decomposition reactions take place during thermal analysis of mixes including HMCs for cement replacements: dehydration, dehydroxylation, and decarbonation of the “included” and “formed” HMCs each (6 reactions), and the decomposition of formed but uncarbonated brucite into MgO (1 reaction). The removal of water of crystallization and decomposition of brucite to MgO within the included HMCs were indicated by the same peak. Although continuous mass loss extended from 100 to 800°C, the results indicated the existence of three or four main DTA peaks, depending on the type of HMC used (i.e. light or heavy), referring to the reactions shown in Table 3. In this context, the “included” HMCs refers to those included as a part of the blends in the initial mixes whereas the “formed” HMCs are those forming as a result of the carbonation process.

The DTA profiles of carbonated phases and carbonates were relatively difficult to evaluate due to a series of overlapping decompositions of substances with a certain level of uncertainty in terms of their stoichiometry. One other challenge of using thermal analysis for the analysis of MgO-cement porous blocks was preparing a sample truly representative of the actual porous blocks. Although the presence of aggregates tends to mask certain features of the results presented at the end of thermal analysis, it has been stated that this does not influence the accuracy of the overall analysis significantly [48]. However, the fact that 90% of the mix making up the porous blocks was composed of aggregates that were hard to break into powder form in preparation for thermal analysis raises up the issue of how representative the chosen small amount of powder (i.e. <50 mg) was of the entire block. For this reason, there is a possibility that the powder originating from the original mix in preparation for the TG/DTA analysis contained more than 10% cement as in the original mix. Although this does not affect the DTA results considerably, the increased cement content overestimates the amount of water and CO₂ within the mixes calculated by using the results obtained by TGA. Since this effect was more pronounced for the degree of hydration calculations due to overlapping steps, thermal analysis was only used to assess the degree of carbonation, the results of which are shown in Fig. 10 in Section 3.5.

Table 3

Steps during the thermal decomposition of mixes containing HMCs

Range of Temperature (°C)	Peak Temperature (°C)	Step	Reaction (e.g. hydromagnesite)
100-350	240-280	Removal of water of crystallization of the included and formed HMC	$4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O} \rightarrow 4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 + 4\text{H}_2\text{O}$
300-400	390-460°C	Decomposition of brucite within the included and formed hydrated HMC to MgO	$4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \rightarrow 4\text{MgCO}_3 + \text{MgO} + \text{H}_2\text{O}$
350-500		Decomposition of the uncarbonated brucite to MgO	$\text{Mg}(\text{OH})_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$
400-600	520-550°C	Decarbonation of included magnesium carbonate to MgO	$4\text{MgCO}_3 \rightarrow 4\text{MgO} + 4\text{CO}_2$
600-1000	750-800°C	Decarbonation of formed magnesium carbonate to MgO	$4\text{MgCO}_3 \rightarrow 4\text{MgO} + 4\text{CO}_2$

(a)

(b)

Fig. 7. XRD patterns of all mixes with MgO:HMC ratios of (a) 1:1 and (b) 4:1

(a)

(b)

Fig. 8. TGA and DTA curves of mixes for all mixes with MgO:HMC ratios of (a)1:1 and (b)4:1

3.5 Quantification of carbon dioxide sequestration

During XRD analysis, degree of hydration is measured by the amount of unhydrated MgO remaining within a certain mix, whereas degree of carbonation is calculated from the amount of uncarbonated brucite. Although the original samples were broken and quartered before being turned into powder form for XRD analysis, use of XRD presents the possibility of the prepared powder not being representative of the parent mix originally containing 90% aggregates, due to similar reasons presented for TG/DTA. Since the cement contents within the prepared powder samples were higher than the corresponding original mixes, XRD was only used to identify the presence of any uncarbonated brucite.

The absence of the brucite peak in all mixes except for LHMC1-50 indicates its full conversion into a range of HMCs, whereas MgO peaks were observed in all mixes. Since complete carbonation of brucite into HMCs was achieved in general, the main potential to improve the overall mechanical performance of the blocks includes focusing on the enhancement of the hydration process. The presence of unhydrated MgO within mixes subjected to carbonation is an indication of either insufficient water required for complete hydration or the difficulty in accessing the present water for the continuation of the hydration process, which is linked with the particle packing arrangement of particles. As shown in a previous study [20], this also brings up the possibility of achieving similar strength results with MgO contents as low as 4%, which would not only reduce the overall cost of producing these blocks commercially but also improve the sustainability of the final product significantly.

The amount of CO₂ absorbed by each mix subjected to accelerated carbonation and natural curing, shown in Fig. 9, was measured by dissolving the samples in HCl acid. In terms of accelerated carbonation, nearly all the mixes achieved 100% carbonation, whereas samples subjected to natural curing carbonated up to 40%. Amongst the naturally cured samples, the control mix revealed the

highest degree of carbonation, which was in agreement with the UCS results, indicating the dependence of strength development on carbonation. There was not a very obvious distinction amongst naturally cured mixes containing HHMC and LHMCs, also consistent with their strength performances presented earlier in Section 3.1. In general, the small amount of CO₂ absorbed by samples during natural curing was an indication of insufficient carbonation within these mixes and hence the low strength results.

The results obtained from the three different methods used to quantify carbonation are presented in Fig. 10, showing the percentage degree of carbonation within samples subjected to accelerated carbonation. The results obtained by TGA, XRD and acid digestion were comparable in general. The amounts of CO₂ sequestered measured by dissolving the samples in HCl acid were slightly higher than the values obtained through other methods, possibly due to the high volatility of the acid and the heat emitted as a result of the rigorous reaction taking place between the carbonated samples and HCl acid. Apart from these slight deviations, all three methods proved reliable in terms of quantifying CO₂ sequestration.

Initially containing 10% MgO and 90% aggregates, the control mix revealed 97% degree of carbonation according to XRD results. Mix LHMC1-50, whose microstructure showed the existence of brucite and no HMCs, illustrated the lowest CO₂ content. On the other hand, mixes HHMC-50, HHMC-20, LHMC1-20, LHMC2-50, and LHMC2-20 containing heavy and light HMCs, demonstrated 100% degree of carbonation, similar to the results obtained by the control mix. However before carbonation can take place fully, all the initially included MgO must be consumed for the formation of brucite during the hydration process. As seen earlier from the XRD results, the presence of MgO indicated an incomplete hydration for most of the mixes, thereby influencing the final performance of the blocks. Only the mixes containing HHMC were able to achieve close to 100% in terms of both the degree of hydration and carbonation. The high conversion rates were also supported by the higher strength results of these mixes, especially HHMC-20, presented in Section 3.1.

Fig. 9. Degree of carbonation of samples subjected to accelerated carbonation and natural curing, obtained by dissolving in HCl acid

Fig. 10. Percentage degree of carbonation of samples subjected to accelerated carbonation measured by thermal analysis, X-ray diffraction, and acid digestion

4. Conclusions

Sequestration of CO₂ within porous blocks through the carbonation of cement formulations including reactive MgO not only provides an efficient solution to carbon capture and storage, but also produces blocks with significant mechanical performance. This paper has addressed the change in microstructure, carbonation progress and strength development of reactive MgO-cement based porous blocks containing a range of HMCs as a part of the cement component. Samples were subjected to two different curing environments: accelerated carbonation (20°C, 70-90% RH, 20% CO₂) and natural curing (20°C, 60-70% RH, ambient CO₂).

The formation of a range of HMCs, including nesquehonite, dypingite, and hydromagnesite was observed as a result of the microstructural analysis of the porous block formulations which were subjected to accelerated carbonation. Mixes subjected to natural curing largely showed evidence of partial hydration with some brucite formation as well as the presence of unhydrated MgO. There was also a small size and content of a structure resembling dypingite/hydromagnesite, indicating a small degree of carbonation, mainly due to the low CO₂ concentration in air. The use of heavy HMC improved the morphology of the mixes by resulting in the formation of nesquehonite, which is favorable due to its prismatic shape that generally forms star like clusters, the main source of microstructural strength.

In addition to microstructure, the use of TG/DTA, XRD, and acid digestion for the quantification of carbonation within the blocks was discussed in detail, providing an insight to support strength development and feedback on the use of each method. Owing to their varying compositions and different methods of production, all HMCs revealed a range of results. In terms of natural curing, the control mix with 10% MgO resulted in the highest strength of 6 MPa after 28 days. Amongst all mixes subjected to 7 days of accelerated carbonation, mixes containing heavy HMC resulted in the highest

strength results of 22 MPa, also demonstrating the highest decrease in porosity due to carbonation. The reason behind this was related to the composition of the heavy HMC, high percentages of degree of hydration and carbonation within the blocks it was used in, along with the formation of nesquehonite at the end of the carbonation process as opposed to other HMCs. The optimum HMC content which would lead to even higher strength results can be identified with further investigation.

This paper has shown that the addition of both heavy and light HMCs has altered the microstructure and carbonation mechanism by resulting in the formation of nesquehonite and dypingite/hydromagnesite particles with larger particle sizes and a different morphology than those of the control mix. It can be concluded that when subjected to the right curing conditions, the use of heavy HMCs can considerably improve the mechanical performance of blocks through extensive hydration, followed by carbonation. They also make it possible to reduce the amount of initial MgO needed to obtain a certain amount of strength, thereby increasing the overall sustainability of the final product by enabling 100% carbonation.

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