The role of brucite, ground granulated blastfurnace slag, and magnesium silicates in the carbonation and performance of MgO cements

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Abstract:

This study focuses on the enhancement of the technical and environmental performance of MgO cements through the inclusion of brucite, GGBS, talc and serpentine as partial MgO substitutes in concrete blocks. The influence of these additives on the microstructure, hydration, carbonation, and mechanical performance of blocks cured under natural and elevated CO₂ conditions is presented. An optimum replacement level was determined for each composition via unconfined compressive strength (UCS), scanning electron microscopy (SEM), x-ray diffraction (XRD), thermogravimetric analysis (TGA) and acid digestion. Mixes subjected to accelerated carbonation indicated up to 100% carbonation in 7 days. Results highlight the suitability of each additive in replacing MgO without compromising performance.

Keywords: Reactive MgO; Microstructure; Thermal analysis; Carbonation; CO₂ uptake; Compressive strength

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1. Introduction

Concrete is the largest volume material used by mankind with an annual consumption volume of around 10 km³. The production of its main component, Portland cement (PC), is responsible for the emissions of 5–8% of global anthropogenic CO₂ and accounts for 12-15% of total industry energy use [1-3]. The significant environmental impacts associated with the production of PC have opened a pathway for the investigation of sustainable alternatives, one of which is the development of cement binders with lower environmental impacts [4, 5]. In this respect, reactive magnesium oxide (MgO) cements, a mixture of reactive magnesia and pozzolans in different proportions depending on the intended application ranging from structural concrete to porous masonry units, have recently emerged as a promising alternative. MgO is produced either naturally from the calcination of magnesium-based minerals (e.g. magnesite and dolomite); or synthetically from seawater, well and lake brines and from chemical precipitation [6, 7]. As listed in Table 1, MgO has a wide range of applications depending on its grade, which is determined by the calcination temperature and conditions used during its production.

The use of reactive MgO as a binder in concrete mixes can present several sustainability advantages owing to its ability to carbonate, leading to a permanent storage of CO₂ accompanied with strength gain [8, 9]. During this process, MgO first hydrates to form magnesium hydroxide (Mg(OH)₂, brucite). The hydrated cement paste absorbs CO₂, which is then chemically combined into carbonate phases within the MgO-CO₂-H₂O system. This process can be applied in a wide range of applications, particularly to prefabricated concrete products that would allow for elevated CO₂ curing for rapid strength development [10, 11]. Hydrated magnesium carbonates (HMCs) such as nesquehonite (MgCO₃·3H₂O), lansfordite (MgCO₃·5H₂O), dypingite (4MgCO₃·Mg(OH)₂·5H₂O), hydromagnesite (4MgCO₃·Mg(OH)₂·4H₂O), and artinite (MgCO₃·Mg(OH)₂·3H₂O) forming as a result of this process [12-14] fill up the available pores and increase the density of concrete mixes due to the volume expansions associated with their formation. The different morphologies and physical properties of each HMC lead to varying abilities in effectively binding the aggregate particles and increasing the overall stiffness of mixes. Although several studies report findings on the factors influencing their formation and properties [15, 16], a complete understanding of the stability and transformation of the products within the MgO-CO₂-H₂O system is yet to be reported.

Table 1
Different grades, properties, and applications of MgO

Grade	Calcination	Reactivity	Specific		Applications
	temperature (°C)		surface area	Crystallinity	
Light- burned (reactive, caustic- calcined)	700-1000	Highest	Highest	Lowest	Catalysts, rubber and paper production, sulfur dioxide removal, fertilizer and animal feed supplements, absorbent for inorganic/organic contaminants, neutralizing agent, filtration medium, agriculture, cattle feed, environmental control, cement [17-24]
Hard- burned	1000-1400	Lower	Lower	Higher	Expansive additive in concrete applications (dam constructions in China) [25]
Dead- burned (periclase)	1400-2000	Even lower	Even lower	Even higher	Refractory applications [26], magnesium phosphate cements [27]
Fused	> 2800	Lowest	Lowest	Highest	Refractory and electrical insulating markets [28]

Within concrete applications involving MgO cements, the rate and degree of carbonation and the associated strength development due to the formation of HMCs are kinetically controlled and depend on the: (i) physical properties and chemical composition of the binder, (ii) mass proportions of the reactants (mix design) [29], (iii) inclusion of additives and admixtures [22], (iv) particle packing and porosity of the

71 hardened concrete [30, 31], and (v) curing conditions (relative humidity (RH), temperature, CO₂
72 concentration and pressure) [15, 32-35]. As a part of a comprehensive study aimed to maximize the
73 sustainability potential of MgO cements, the main focus of this study is on the use of certain cement
74 replacements to enhance the CO₂ sequestration capability of reactive MgO porous masonry blocks by
75 increasing the hydration and carbonation degrees up to 100%. To achieve this, certain proportions of
76 MgO were replaced with brucite, GGBS, and magnesium silicates (talc and serpentine).

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78
79 Brucite has several industrial applications including its use in pulp and paper production, pharmaceutical
80 industry, wastewater treatment, flame retardants, and smoke-suppressing additives. It is commonly
81 obtained by hydrating magnesia as seen in Equation 1. The hydration mechanism follows these steps: (i)
82 adsorption of water at the surface and its simultaneous diffusion inside porous MgO particles, (ii)
83 dissolution of oxide within these particles, changing porosity with time, and (iii) creation of
84 supersaturation, nucleation and growth of brucite at the surface of magnesia [36]. The type of the
85 precursor and the kinetics of this reaction directly influence the quality and the properties of the end
86 product [37-39]. During this process, a layer of newly formed brucite forms on the surface of magnesia,
87 imposing an additional resistance that limits the further continuation of the hydration process. In the case
88 of applications involving MgO cements, this mechanism presents a constraint on the progress of
89 hydration and the subsequent carbonation process, hindering the strength development of mixes. Small
90 replacements of MgO with brucite can potentially accelerate the carbonation process and eliminate any
91 delayed hydration should that occur, especially when MgO of lower reactivity is used, by acting as an
92 intermediate step during the carbonation of MgO within porous applications.

98 Brucite introduced to the mix during the initial mixing stage can act as seed crystals for the newly formed
99 carbonates and provide nucleation sites for enhanced hydration. A study by Thomas et al. (2009) [40]
100 demonstrated significant acceleration of early hydration kinetics by providing nucleation sites for the
101 precipitation of hydration products through small additions of calcium-silicate-hydrate (C-S-H) to PC and

tricalcium silicate (C_3S) pastes. Formation of C-S-H gel, the main binding phase, was seeded, providing new nucleation sites within the pore space. This significantly increased the early hydration rate and total amount of hydration during the early nucleation and growth period within the first 24 hours. Similarly, this study aims to investigate the capability of brucite addition in altering the hydration mechanism of MgO cements by reducing the formation of brucite film on the MgO surface, leading to unimpeded hydration, and facilitating the formation of $Mg(OH)_2$ crystals with different physical and microstructural properties. Formation of brucite crystals with a rosette-like morphology where plates are connected to each other at an angle can create spaces between the plates, increasing the surface area exposed to carbonation and providing extra room for the formation of further carbonates.

Ground granulated blastfurnace slag (GGBS) is a by-product of the steel industry. During the manufacture of iron, iron-ore, coke and limestone are fed into the blastfurnace, whereby the iron-ore is reduced to iron, which separates out from the remaining slag. The slag is then tapped off and cooled rapidly to retain its cementitious properties. It is then dried and finely ground to a fineness similar to that of PC to facilitate its use as a cementitious material. Used as a component of blended cement or as a supplementary cementing material to improve the long term properties of concrete and reduce the overall carbon footprint, slags have similar chemical compositions to PC [41, 42]. As GGBS is a by-product, it has a much lower carbon footprint than PC (0.055 vs. 0.85 tonne of CO_2 is emitted per tonne of GGBS and PC [43], respectively). Therefore, replacement of one tonne of clinker by an equivalent amount of slag facilitates the reduction of about 800 kg of CO_2 emissions [44, 45].

Although the addition of GGBS can slow down the reaction and retard the setting time of concrete [46], it was observed that when it was incorporated with fly ash, the hydration rate of fly ash and GGBS increased at the early ages [47]. The increased hydration rate of GGBS with high CaO and MgO contents was attributed to its large specific surface, which facilitated the formation of further nucleating sites and OH^- ions as well as alkalis into the pore fluid. Both the OH^- ions and alkalis react with SiO_2 and break down the glass phase of fly ash, which, as a result, accelerates the process of hydration. In PC mixes, GGBS reacts with $Ca(OH)_2$, forming a secondary calcium silicate compound. Homogeneous hydration products such as ettringite and $Ca(OH)_2$, which have larger specific surfaces than PC, can also form. The

secondary calcium silicate, ettringite and Ca(OH)_2 act as nucleating sites, resulting in an increased hydration rate [47].

The inclusion of GGBS in reactive MgO systems can have a similar effect where MgO can serve as an alkali activator and hence accelerate the hydration process [48]. The effectiveness of activation and the hydration of the slags are mainly influenced by the mineralogical composition and fineness of the slag and on the type of the alkaline activator used. The major hydration products are C-S-H and hydrotalcite-like phases ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$), whereas the content of the latter increases with MgO content and reactivity [49]. The influence of MgO in alkali-activated slag systems has been reported by several studies, either internally within the slag composition [50, 51], or externally as an additive [52]. The effective activation capability of MgO when introduced with GGBS due to its alkaline nature was reported to improve the overall microstructure via the generation of voluminous hydration products [48, 52] and result in high reaction and strength levels [53]. As the reactivity and composition of the MgO influences the overall strength development, it must be highlighted that the internal MgO within the GGBS composition (i.e. usually produced between 1400-1600°C [54]) is vitreous and is often present as a crystalline mineral such as spinel (MgAl_2O_4) or åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$); whereas the externally added MgO is usually reactive grade (i.e. calcined under 1000°C).

The worldwide reserves of magnesium silicates such as serpentine and olivine are in excess of 10 trillion tonnes [55]. Serpentine ($3\text{MgO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$) is a general name applied to several members of a polymorphic group composed of SiO_2 (>45 %), MgO (>30%), and Fe-oxides (>10%). It usually exists in compact masses as a major rock forming mineral and is found as a constituent in many metamorphic and igneous rocks. Serpentine is a suitable raw material for the production of high-purity MgO and silica. Its structure is composed of layers of silicate tetrahedrons with imperfect layers of brucite in between with a tendency to bend. The carbonation of serpentine traps CO_2 as environmentally stable solid carbonates (e.g. magnesite) [56, 57]. Similarly, talc is a hydrated magnesium silicate with the chemical formula $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ or $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ($3\text{MgO}\cdot 4\text{SiO}_2\cdot \text{H}_2\text{O}$). The crystal structure of pure talc contains brucite sheets in between silica sheets, forming superimposed talc layers. It is widely used in paper making, plastics, paints, rubbers, pharmaceuticals, cosmetics, ceramics, and food processing industries. It is

extracted from more than 250 deposits scattered across the globe and has an annual worldwide production of around 560,000 metric tons [58]. Talc deposits result from the transformation of existing rocks under the effect of hydro-thermal fluids carrying the components needed to form the mineral (MgO and SiO_2). Mostly formed from the alteration of dolomite or magnesite in the presence of excess dissolved silica, talc deposits differ according to their parent rock. Talc and serpentine are included in the MgO cement formulations prepared under this study to investigate their potential benefits on the enhancement of the carbonation of porous blocks.

This study focuses on the enhancement of the technical and environmental performance of MgO cements through the inclusion of brucite, GGBS, talc and serpentine as a partial substitute of MgO . The capability of each additive in advancing the hydration and carbonation processes is shown by quantitative results, indicating their performance in blocks. The objectives of this work are to:

- (a) Investigate the influence of these additives as a part of the cement component on the hydration and carbonation of MgO cements by providing a quantitative analysis on the extent of hydration and carbonation of blocks with different compositions using various methods (i.e. TGA, XRD, and dissolving in HCl acid).
- (b) Provide a comparison of blocks cured under accelerated and natural CO_2 conditions in terms of the degree of carbonation, strength and microstructural development.
- (c) Examine the effect of different water contents in enhancing the strength and hence degree of carbonation for each mix.
- (d) Make recommendations on the suitability of each additive in replacing MgO without compromising mechanical performance.

2. Materials and methods

2.1. Materials, sample preparation, and curing

The reactive magnesium oxide used was grade 94/325 obtained from Richard Baker Harrison, UK. The additives included brucite (from Richard Baker Harrison, UK), GGBS (from Civil and Marine, UK), talc (from Sigma-Aldrich, UK), and serpentine (from Richard Baker Harrison, UK). The cement content, including reactive MgO and additives, was kept constant at 10% of the dry mix. Pulverized fuel ash (PFA), obtained from Ratcliffe-on-Soar power station in Nottingham, UK, was used as a filler. Addition of PFA as a partial replacement for cement not only reduces the amount of cement used, but also provides a solution for recycling this industrial by-product, therefore lowering the overall environmental impacts of the prepared mixes. In our previous studies [35], it was shown that including small amounts of PFA helped endure the dry environments and resulted in strength results four times higher than those mixes where it was completely eliminated. The chemical composition of the MgO, PFA, and GGBS are presented in Table 2. As used in previous related work [29, 30], natural aggregates consisting of sharp sand (0-4mm, median particle diameter (D_{50})= 0.7mm, coefficient of uniformity (C_u)= 3.6) and gravel (2-10mm, with D_{50} = 6.5mm, C_u = 1.75) were used together at 50% and 35% of the dry mix content, respectively,

The dry powders of MgO, additives, 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 additives contained 85% natural aggregates, 5% PFA, and 10% cement which was composed of MgO:additive at different ratios. The control mix used was composed of 10% MgO alone for the cement content, and the water content was optimized in a previous study [35] at a water to cement (w/c) ratio of 0.8 for the highest strength. All the different mix compositions tested under this study, along with the corresponding standard consistency (SC) of each mix from which the w/c ratios were derived, are listed in Table 3.

Table 2

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	Mean diameter (μm)	Specific Surface area (m ² /g)	Loss on ignition (%)
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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
GGBS	39.5	36.5	0.5	12.5	8.5	-	35.0	5-30	-
Talc	0.6	59.3	1.0	1.9	31.5	-	-	-	5.5

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224 Equal weights of the prepared mixes were placed in metal cylindrical molds 50mm in diameter and the
225 samples were then produced in a laboratory uni-axial press by applying a previously optimized force of 5
226 kN. The produced samples, 70-75mm high, were then immediately de-molded and placed in the relevant
227 curing environments. Two main curing conditions were used: (i) natural curing (20°C, 60-70% RH, and
228 ambient CO₂) for 28 days, and (ii) accelerated carbonation curing (20°C, 70-90% RH and 20% CO₂
229 concentration) in an environmental incubator for 7 days.

230

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232 Table 3

233 Composition of the mixes produced

Additive	Mix no.	Cement (%)		Water/cement ratio	SC	of
		MgO	Additive	(Optimum w/c in bold)	pastes	
Control	C	10	0	0.80	0.60	
Brucite	B-50	5	5	0.63, 0.67, 0.70 , 0.73, 0.77	0.47	
	B-100	0	10	0.49, 0.53, 0.56 , 0.60, 0.65	0.40	
GGBS	G-50	5	5	0.60, 0.68, 0.75 , 0.79, 0.82	0.45	
	G-80	2	8	0.49, 0.56, 0.63 , 0.69, 0.70	0.37	
Talc	T-50	5	5	0.71, 0.75, 0.80, 0.83 , 0.86	0.73	
	T-20	8	2	0.72, 0.75, 0.78, 0.80 , 0.84	0.62	
Serpentine	S-50	5	5	0.63, 0.67 , 0.70, 0.73	0.56	
	S-20	8	2	0.74, 0.78 , 0.82, 0.86	0.60	

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236 **2.2. Experimental testing procedures**

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239 The SC of MgO and the additives were measured according to BS EN 196-3:2005+A1:2008 [59]. The
240 unconfined compressive strength (UCS) was measured by uni-axial loading of the samples in triplicates.
241 The microstructure of representative samples from outer surface of the samples was observed by
242 imaging fracture surfaces under scanning electron microscopy (SEM), JEOL JSM-5800 LV, facilitating
243 elemental composition analysis. Three different methods were used for the quantification of carbonation:
244 (i) X-ray diffraction (XRD), (ii) thermogravimetric analysis (TGA), and (iii) HCl acid digestion. X-ray
245 diffraction (XRD), conducted on a Siemens D500 Diffractometer, was utilized to provide qualitative and
246 quantitative analyses of the crystalline phases present within the mixes. The samples were broken down
247 to small pieces (<5mm) and then quartered before being ground down to 125 μ m to be analyzed under
248 XRD. The relative diffraction peaks of MgO, Mg(OH)₂, additives, and HMCs in each mix were identified by
249 using X-ray diffraction analysis under the operating conditions of Cu K α radiation (40 kV, 40 mA); scan
250 rate: 2°/step; 2 θ : 5-50°. The Reference Intensity Ratio (RIR) technique [60-64] was applied for the
251 quantitative analysis of the phases present by making use of a standard phase with a known proportion,
252 whose integrated intensity was compared to that of the phase of interest. The internal standard used for
253 quantification purposes was fluorite (CaF₂) at 20 wt% [65]. Calibration curves for magnesia and brucite,
254 which were the components used for the purposes of quantitative analysis, were straight lines through the
255 origin i.e. $y=kx$, where x is the RIR of the phase analyzed and y is the weight fraction of the component
256 investigated. The value of k was 0.2886 for magnesia and 0.3651 for brucite [66]. The RIR was acquired
257 through dividing the integrated intensity of the strongest line of the phase with that of the standard.
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260 The thermogravimetric analysis instrument used was a Perkin Elmer STA 6000, controlled by Pyris
261 software. Initially the sample powder was obtained using a 75 μ m sieve. To start the analysis, the powder
262 was placed in a crucible designed to be used in the TGA instrument, where the samples were heated in
263 air from 40°C to 1000°C at a rate of 10°C/minute. The change in mass with the increasing temperature
264 was recorded to provide qualitative and quantitative information. Another method to measure the amount
265 of CO₂ absorbed during carbonation was by acid digestion using hydrochloric (HCl) acid, which involved
266 neutralization of solutions containing CO₂ and chemical decomposition of the carbonates through their
267 reaction with the acid. A 3M/l HCl acid solution was prepared by diluting concentrated HCl acid (initial
268 concentration of 37.5%) with distilled water. This relatively high molarity caused the reaction to take place

within a few minutes, thereby providing rapid results without incorporating the volatility of the acid solution. The samples were also broken down into small pieces to reduce the overall reaction time, explained by the following reactions:

3. Results and discussion

3.1. Thermal decomposition of cement additives

The TGA and Differential Thermal Analysis (DTA) graphs for MgO and additives are shown in Fig. 1. TGA results indicated a total of 6.15% impurity level for MgO. Brucite demonstrated a single peak at 412°C, referring to its decomposition into MgO. Around 31% of the total weight of brucite was lost during thermal analysis, corresponding to the percentage of water within brucite. GGBS had a small peak at 690°C, corresponding to 0.7% loss in mass. Talc, which contains adsorbed water and water in the form of hydroxyl groups [67], experienced a mass loss of 1.2% at 570°C. During its thermal decomposition, an endothermic peak due to the loss of the adsorption water occurs at 100-500°C [68], without changing the crystal structure or properties of the mineral. Three stages of talc dehydration are reported at 120-200°C, 350-500°C, and 600-1050°C. Following the loss of water during the first two stages, the third stage of mineral dehydration involves the liberation of non-hygroscopic water, at the end of which talc is decomposed into free MgO and silica [69, 70]. Since talc was subjected up to 800°C during the thermal decomposition shown in Fig. 1, all the water may not have liberated during this process. Serpentine is made up of SiO₂ (>45 %), MgO (>30%) and Fe-oxides (>10%). Alternate half-layers of silicate and brucite are present with a misfit between two half-layers, which produces a curvature of the lattice with the brucite on the outside [71]. A total of 4.5% weight loss was observed during its thermal analysis, whose

main peaks were at 593°C and 689°C. The endothermic peak at 689°C indicates the decomposition of the crystal lattice of the serpentine powder.

Fig. 1. TGA and DTA curves of additives

3.2. Performance of blocks with cement replacements

3.2.1. Standard consistency

The SC of each additive, along with those of MgO and PFA, is shown in Fig. 2. Talc has the highest SC at 0.78 amongst all additives, resulting in mixes with high water demands, whereas GGBS has the lowest SC of 0.31. The SC values of MgO and serpentine are very similar, explaining the similarity between the optimum w/c ratios of the control mix (0.80) and those of S-50 and S-20 mixes, which were 0.67 and 0.78, respectively. The optimum w/c ratio required for the highest strength results was ~30-50% higher than the corresponding SCs for most compositions, whereas it was around ~30% for the control mix. This increase

was lower at ~15-30% for samples including talc and serpentine depending on the replacement ratio, validating their compatibility within the proposed formulations. PFA and brucite both have very similar SCs, reducing the overall water demand of mixes they were included in. The lower amounts of water demanded by most of these materials to achieve SC while maintaining mechanical performance can present a sustainability benefit if implemented on a large scale.

Fig. 2. Standard consistency of the cement replacement additives used

3.2.2. Unconfined compressive strength

UCS values of all samples subjected to 7 days of accelerated carbonation are shown in Fig. 3 and 4. The amount of water included in MgO systems subjected to carbonation plays an important role in the permeability of mixes, which influences the diffusion of CO₂. Gaseous CO₂ readily dissolves in the pore water and reacts with magnesium hydroxide to form a range of strength providing HMCs. Water helps

with the initial compaction and provides a medium for carbonation to take place, explaining the initial increase in the strength results as the amount of water in the pore structure increases. Any excess water not utilised during this process hinders CO₂ diffusion by blocking the available pores, therefore leading to the reductions in strength values. Therefore, an optimum water content that led to the highest strength was aimed for each composition.

Fig. 3(a) shows that MgO replacement by brucite achieved strength results between 13.2-18.5 MPa. Mixes where brucite replaced 50% of MgO (B-50) produced higher strength results than those containing only brucite as the binder (B-100). Mix B-50 with w/c of 0.70 achieved the same strength results (18.5 MPa) as the control mix containing only MgO (18.2 MPa), showing that replacing MgO with a certain percentage of brucite does not compromise the strength. Even higher strengths could possibly be obtained if smaller amounts of brucite (<5% by weight of the total mix) are used, as long as carbonation and the dense formation of HMCs take place.

The strength development of mixes containing GGBS is shown in Fig. 3(b). Carbonation of G-50 mixes led to strengths as high as 15.6 MPa, whereas this was much lower at 6.7 MPa for G-80 mixes, both lower than the control mix. Contrary to other studies, which report an acceleration in both the hydration and pozzolanic reactions of PC with the inclusion of GGBS [47], and those where MgO is used as an alkali activator of GGBS [48], leading to high strengths; the inclusion of GGBS within porous block applications subjected to accelerated carbonation did not indicate the same effect. This is mainly because a majority of the MgO used within these mixes was carbonated and therefore was not available to activate GGBS. Any hydration products that formed as a result of the activation of GGBS with MgO carbonated as well, yielding calcium and magnesium carbonates along with silica gel. Therefore, the anticipated strength gain due to the activation process has not been observed.

Mixes T-50 and T-20, involving partial replacements of MgO by talc as shown in Fig. 4(a), achieved highest strengths of 8.3 MPa and 17.9 MPa, respectively. An optimum w/c of ~0.80 was observed in both cases, similar to the control mix. Including 2% talc with 8% MgO led to strengths almost as high as the

control mix, showing that talc can partially replace MgO without hindering the strength development. This can also present an economical benefit due to the possibly lower market value of talc (ranging between \$100-\$1000 per tonne depending on the purity and fineness of the powder) when compared to that of MgO (~\$470 per tonne). Additionally, owing to the common occurrence of magnesium silicates across the world and lower energy requirements during their production, the use of talc can reduce the overall carbon footprint of the blocks without sacrificing mechanical performance. Shown by Fig. 4(b), the use of serpentine at two different ratios, S-50 and S-20, resulted in strengths of 17.8 MPa and 17.0 MPa, respectively. Unlike other additives, strength of mixes increased with higher serpentine content, defining serpentine as one of the most feasible substitutes of MgO. Considering the high stability and low reaction potential of serpentine under the curing conditions presented in this study, the strength retention can be attributed to the lower water contents of mixes S-50 and S-20.

Fig. 5(a) and (b) show the overall strength results of all mixes over a range of water contents after 7 days of accelerated carbonation and 28 days of natural curing, respectively. Amongst all mixes subjected to natural curing, the control mix achieved the highest strength result, 6.1 MPa, indicating a limited amount of carbonation. However, previous studies have shown that 28 days is a relatively short period for carbonation to take place under natural conditions, and continuous strength gain can be observed if the blocks are cured for longer durations [30].

Similar to accelerated carbonation, mixes B-50 and G-50 achieved the highest strength results (4.0 MPa) amongst all mixes including additives under natural curing. Although the inclusion of GGBS was not favorable within samples subjected to accelerated carbonation, it had a different effect under lower CO₂ concentrations (0.039% vs. 20%). When MgO carbonated under accelerated CO₂ conditions, it could not react with GGBS, which is a latent hydraulic material unless activated for strength gain. However under ambient conditions, MgO was available to act as an alkali activator for GGBS as carbonation did not take place immediately due to the low CO₂ concentrations. The effective activation capability of MgO when introduced with GGBS due to its alkaline nature was reported to result in high reaction and strength levels [53]. Owing to its lower costs than MgO, GGBS presents itself as an economical binder and can replace MgO up to a certain extent within formulations subjected to natural curing conditions.

(a)

(b)

Fig. 3. UCS of mixes including (a) brucite and (b) GGBS

(a)

(b)

Fig. 4. UCS of mixes including (a) talc and (b) serpentine

(a)

(b)

Fig. 5. UCS of mixes at (a) 7-day accelerated carbonation, (b) 28-day natural curing

3.2.3. Microstructure

SEM images of the control mix subjected to accelerated carbonation and natural curing are shown in Fig. 6(a) and (b), respectively. An abundant formation of rosette-like hydromagnesite/dypingite was observed

after 7-days of accelerated carbonation. These HMCs form well-ramified networks of massive crystals with a very effective binding ability, explaining the strength gain. Alternatively, individually fused brucite particles were seen in the case of natural curing, denoting the incomplete carbonation process. In addition to brucite, formation of a HMC similar to hydromagnesite/dypingite was observed, explaining the relatively high strengths obtained by the control mix after 28-days of natural curing.

(a) (b)
Fig. 6. SEM micrographs of control mix after (a) 7-days of accelerated curing, (b) 28-days of natural curing

SEM images of samples containing brucite and GGBS replacements subjected to 7-days of accelerated carbonation are shown in Fig. 7(a)-(d). Similar to the control mix, rosette-like crystals of hydromagnesite/dypingite were observed after the carbonation of B-50 and B-100, with an apparent difference between the HMCs forming in each case. Carbonation of B-50 led to the formation of dense hydromagnesite/dypingite particles fused into larger agglomerates; whereas B-100 indicated the presence of individual particles which mostly resembled dypingite [72]. Therefore, complete replacement of MgO with brucite resulted in variations in the formation of HMCs, also confirmed by the X-ray diffractograms showing the phases present in each formulation in Section 3.2.4. In addition to the variably-sized spherical PFA particles, presence of brucite particles is observed in G-50 and G-80 mixes, explaining the lack of complete carbonation and hence the relatively low strength results obtained. The microstructures of samples including talc and serpentine after accelerated carbonation are shown in Fig.

8(a)-(d). A vast content of talc and brucite is observed in T-50, whereas the dense formation of nesquehonite was seen in the case of T-20, explaining the much higher strength results of the latter (8.3 MPa vs. 17.9 MPa). Mixes S-50 and S-20 containing serpentine, which resulted in very similar strength developments, displayed a well-ramified dense network of elongated nesquehonite crystals. Although the hardness of nesquehonite and brucite is similar at ~2.5 [73], it is the monolithic nature of the former due to which the systems with nesquehonite are much stronger. No other HMCs were observed under SEM, suggesting the domination of nesquehonite as the main carbonation product of mixes incorporating silicates with MgO.

Fig. 9 and 10 show the microstructures of all samples after natural curing. The common component in all micrographs is brucite, revealing that even though hydration took place, carbonation of the samples was not completed after 28-days of natural curing, as expected. Mix B-50, which achieved the strongest strength after the control mix, showed limited formation of nesquehonite that contributed to the strength development. This was not the case for mix B-100, where only brucite was observed with no HMCs, resulting in strengths less than 1 MPa. A limited formation of hydromagnesite/dypingite was observed for mix G-50, which may have contributed to the strength gain. Mixes involving talc and serpentine demonstrated similar strength and microstructural developments, where those with 20% cement replacements performed better than those with 50% replacement levels. Although a network of brucite particles was seen in all mixes, indicating little carbonation, mixes with talc displayed plate-like irregular crystals very similar to those of hydromagnesite/dypingite.

(a)

(b)

(c)

(d)

Fig. 7. SEM micrographs after accelerated carbonation of mixes (a) B-50, (b) B-100, (c) G-50, (d) G-80

(a)

(b)

(c)

(d)

Fig. 8. SEM micrographs after accelerated carbonation of mixes (a) T-50, (b) T-20, (c) S-50, (d) S-20

(a)

(b)

(c)

(d)

Fig. 9. SEM micrographs after natural curing of mixes (a) B-50, (b) B-100, (c) G-50, (d) G-80

(a)

(b)

(c)

(d)

Fig. 10. SEM micrographs after natural curing of mixes (a) T-50, (b) T-20, (c) S-50, (d) S-20

3.2.4. XRD

As samples subjected to natural curing did not show major indications of carbonation, XRD and TGA were applied to the samples subjected to accelerated carbonation. X-ray diffractograms of mixes including brucite and GGBS are shown in Fig. 11(a) and (b), respectively. The XRD data of the control mix is also included for comparison purposes. The fluorite (F) peak at 28.25° 2Theta is used as an internal standard for the hydration and carbonation quantification. The absence of brucite peaks in all mixes except for the control, B-50 and B-100, which contained brucite to start with, confirmed that brucite was fully converted to various HMCs with the inclusion of additives. The high extent of carbonation in all mixes was shown by the prominent peaks of different HMCs, including hydromagnesite, dypingite and nesquehonite. However, the presence of MgO peaks was an indication of incomplete hydration. The main characteristic peak of the included brucite at 18.7° and 38.0° 2Theta was abundant even after the carbonation of mixes B-50 and B-100. Alternatively, the control mix indicated much lower peaks of brucite when compared to these mixes, indicating a high degree of carbonation. The absence of MgO and brucite peaks within G-80 was due to the complete carbonation of the small amount of MgO used in this mix, in line with the findings of Yi et al. (2012) [53]. When compared to other mixes, peaks of nesquehonite were much smaller within mix G-80. Dypingite and hydromagnesite seemed to be the main HMCs forming due to carbonation. Any hydration products that formed as a result of the activation of GGBS carbonated as well, explaining the inability of activation to contribute to the overall strength gain.

(a)

(b)

Fig. 11. X-ray diffractograms of mixes including (a) brucite, (b) GGBS

(a)

(b)

Fig. 12. X-ray diffractograms of mixes including (a) talc, (b) serpentine

3.2.5. Thermal analysis

Decomposition of mixes including a range of additives was studied by plotting percentage weight against temperature on the TGA curve, whereas DTG was used to study the origin of the peaks forming during this process. The peak temperatures and the temperature ranges during which each decomposition step took place are listed in Table 4. The relatively small amount of weight loss taking place at $<120^{\circ}\text{C}$ was due to the hygroscopic water. The control mix illustrated two distinct endothermic peaks. The first peak at 411°C referred 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 referred 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 HMCs.

The TGA and DTG curves of all mixes are presented on Fig. 13 and 14. In the case of mixes including brucite as the cement additive, three main endothermic peaks were observed at ~430°C, 540°C, and 785°C. As seen in Fig. 1, the decomposition of the brucite included within the mixes took place at a peak temperature of ~412°C. Therefore, the first of the three endothermic peaks in the case of B-50 and B-100 at ~430°C refers to the decomposition of the brucite into MgO, taking place between 350-490°C. This includes (i) any residual brucite included initially as an additive, (ii) brucite formed as a result of the hydration of MgO but was uncarbonated in mix B-50, and (iii) dehydroxylation of brucite within the formed HMCs. Since mix B-100 contains more brucite than B-50, the higher weight loss obtained at this temperature in the case of mix B-100 is as expected. In addition to the decomposition of brucite, the weight loss during the peak at ~430°C includes the removal of water of crystallization within the formed HMCs.

The second peak at 540°C was attributed to the addition of brucite in the system as it was not observed in the control mix. Impurities present within MgO and PFA, whose thermal decomposition alone indicated a peak at ~550°C and resulted in a weight loss of 3.35% and 6%, respectively, may have contributed as well. Although not as pronounced, this peak was present in all the mixes involving MgO and PFA, confirmed by samples tested in triplicates. The appearance and size of this peak depend on several factors, including sample size and composition, and heating rate. Finally, the last endothermic peak at 785°C corresponds to the decarbonation step during which MgCO_3 decomposes into MgO.

Although following the same trend, the three steps of dehydration, dehydroxylation, and decarbonation took place at much higher temperatures than those stated by Botha and Strydom (2003) [74] and Choudhary et al. (1994) [75], for whom these reactions were observed at <250°C, 250-350°C, and >350-550°C. This could be due to the different routes used during the production of HMCs in these studies (i.e. commercial production and through the precipitation of magnesium salts), whereas HMCs forming as a result of the carbonation of MgO cements decompose at much higher temperatures. This was confirmed in earlier studies [12], where the decomposition of seven different commercially obtained HMCs was studied in detail and compared with HMCs formed via the carbonation of MgO cement formulations.

Thermal decomposition of mixes including GGBS demonstrated a similar trend to those with brucite. In addition to the loss of evaporable and bound water at <120°C, three endothermic peaks were observed at 430°C, 580°C, and 790°C. These peaks correspond to the dehydration and dehydroxylation of HMCs, decomposition of the impurities within MgO and PFA, and decarbonation of HMCs, respectively. Mixes with talc and serpentine had two distinct peaks at ~450°C and 770°C, the first one referring to the dehydration and dehydroxylation steps, whereas the latter was due to decarbonation. Although small, minor weight losses observed during the thermal analysis of talc and serpentine as seen in Fig. 1 also contributed to these peaks. In all mixes, the HMCs forming as a result of carbonation decomposed fully within the range of 660-840°C, at the end of which MgO was left as the final product.

Although it provides a good understanding of the steps involved during the thermal decomposition of carbonated MgO cement mixes, the TGA data was only used for carbonation quantification and not in the determination of hydration degrees within the prepared blocks. This is because the DTA profiles of brucite and carbonated phases were difficult to evaluate due to a series of overlapping decompositions. This presented a difficulty in separating the weight loss caused by the dehydration of HMCs and the decomposition of brucite into MgO, both of which took place during the same peak.

Table 4
Thermal decomposition of mixes containing cement additives

Mix	Temperature Range (°C)	Peak Temperature (°C)	Weight Loss (%)
Control	350-490	411	11.1
	600-800	748	7.5
	350-470	423	4.2
B-50	515-560	535	1.4
	680-840	792	4.1
B-100	350-490	430	9.7

	520-570	540	3.3
	680-840	785	6.2
	380-490	436	5
G-50	560-620	588	0.7
	690-840	785	7.5
	390-450	422	1.2
G-80	550-640	583	1.1
	680-850	790	7.1
	350-490	451	7.7
T-50	650-830	788	7
	350-510	442	10.7
T-20	650-830	776	5.5
	340-500	450	11.9
S-50	650-800	760	6.3
	360-500	445	11.4
S-20	650-800	773	4.9

Fig. 13. TGA and DTG curves of mixes including (a) brucite, (b) GGBS

(a)

(b)

Fig. 14. TGA and DTG curves of mixes including (a) talc, (b) serpentinite

3.2.6. Quantification of hydration and carbonation degrees

TGA, XRD and acid digestion were used to quantify the amount of CO₂ within the mixes investigated under this study. MgO contents within each mix are listed in Table 5, whose last column indicates the total amount of MgO, including that incorporated within the cement additives. MgO contents within serpentine and talc were calculated as 43.5% and 31.8%, respectively. After the control mix with 10% MgO, mixes S-20 and T-20 had the highest MgO content, which were 8.9% and 8.6%, respectively.

Table 5
MgO contents within mixes containing cement additives

Mix	Initial MgO Content (%)	Total MgO Content (%)
Control	10	10
B-50	5	5
B-100	0	0
G-50	5	5
G-80	2	2
T-50	5	6.6
T-20	8	8.6
S-50	5	7.2
S-20	8	8.9

While the presence of aggregates does not influence the accuracy of the overall TGA significantly [76], the fact that 85% of the block composition included 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 (usually <50 mg) was of the entire block. From the TGA results obtained, it was concluded that the samples used for thermal analysis were not truly representative of the actual parent block in terms of

composition since the powder originating from the original mix in preparation for the TGA analysis contained more than 10% cement as in the original mix. Although this does not affect DTG results, the increased cement content can lead to an overestimation of the degree of hydration and carbonation within the mixes calculated by TGA results.

The weight fractions of the relevant phases obtained by XRD analysis for all the mixes, along with the degree of hydration (i.e. derived from the amount of MgO left unhydrated) and carbonation (i.e. derived from the amount of brucite left uncarbonated) used to calculate the degree of MgO conversion (i.e. computed by multiplying the degree of hydration with the degree of carbonation, therefore taking both processes into account) are shown in Table 6. No brucite was observed in most of the samples after carbonation, indicating that all the brucite which initially formed due to the hydration of MgO had been fully consumed during carbonation. The degree of hydration varied between 70-100% amongst all mixes, followed by full carbonation in most cases. Mix B-50, which performed better than the control mix indicated a smaller degree of carbonation than most mixes. Mix G-80, which resulted in the lowest strength results experienced complete hydration and carbonation (i.e. no MgO or brucite peaks were observed), purely because of the small MgO content (2%) to start with. Overall, these results indicate that: (i) the degree of hydration and carbonation is not necessarily the only factor affecting the final mechanical performance of applications involving MgO cements, and (ii) other factors such as the type, properties, and interaction of the individual HMCs forming as a result of this process play an important role in the determination of overall performance.

Table 6

Content of the crystalline phases obtained by XRD analysis and the related degree of hydration, carbonation and MgO conversion

Mixes	MgO (w/w)	Brucite (w/w)	Degree of Hydration (%)	Degree of Carbonation (%)	Degree of MgO Conversion (%)
Control	0.009	0.004	91	97	88
B-50	0.005	0.04	90	46	42

G-50	0.02	0	70	100	70
G-80	0	0	100	100	100
T-50	0.02	0	70	100	70
T-20	0.015	0	83	100	83
S-50	0.01	0	86	100	86
S-20	0.013	0	85	100	85

The carbonation degree of each mix subjected to accelerated carbonation and natural curing, shown in Fig. 15(a), 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%. Mixes containing brucite and GGBS indicated smaller amounts of carbonation than the rest, although mix B-50 produced strengths higher than the control mix. Amongst the naturally cured samples, the control mix revealed the highest degree of carbonation, which was in agreement with the UCS results.

The results obtained from all three methods are presented in Fig. 15(b), which represents the degree of carbonation of samples subjected to accelerated carbonation. The results obtained by each method were comparable for most mixes. 100% carbonation was observed in the control mix and those with talc and serpentine, whereas mixes containing brucite and GGBS carbonated less. Mixes B-50 and B-100 indicated ~50% and 80% carbonation, respectively. The fact that smaller degrees of carbonation were obtained for these mixes by each of the three methods confirms that even though carbonation degree is an indication of strength gain, there are other governing factors influencing the overall mechanical performance of MgO cement mixes.

(a)

(b)

Fig. 15. Degree of carbonation obtained by (a) dissolving samples in HCl acid after accelerated and natural curing, (b) three different methods after accelerated carbonation

4. Conclusions

The main focus of this study is the use of certain cement replacements to enhance the CO₂ sequestration capability of reactive MgO masonry blocks. Certain proportions of MgO were replaced with brucite, GGBS, and magnesium silicates (talc and serpentine) under natural and accelerated CO₂ concentrations, generating the following conclusions on each additive:

(i) Brucite: Small replacements of MgO with brucite have the potential to accelerate the carbonation process by acting as seed crystals and providing nucleation sites for enhanced hydration. This can eliminate any delayed hydration should that occur by presenting an intermediate step during the carbonation of MgO within porous applications. A change in the hydration mechanism was expected due to the reduction of the formation of brucite film on the MgO surface, leading to unimpeded hydration and facilitating the formation of Mg(OH)₂ crystals with different physical and microstructural properties. The results indicate that mixes where brucite replaced 50% of MgO achieved the same strength results as the control mix, even though the carbonation degree was lower (46% vs. 97% obtained by XRD-RIR analysis). The maintenance of mechanical performance was attributed to the formation of dense hydromagnesite/dypingite particles fused into larger agglomerates with a rosette-like morphology, showing that replacing MgO with a certain amount of brucite does not compromise the strength. Even higher strengths could possibly be obtained if smaller amounts of brucite were used, as long as carbonation and the dense formation of HMCs take place by increasing the surface area exposed to carbonation and providing extra room for the formation of further carbonates.

(ii) GGBS: As GGBS is a by-product, it has a much lower carbon footprint than MgO. It can facilitate the formation of further nucleating sites and OH⁻ ions as well as alkalis into the pore fluid. The effective activation capability of MgO when introduced with GGBS due to its alkaline nature was reported to improve the overall microstructure via the generation of voluminous hydration products and result in high reaction and strength levels. This study shows that replacing 50% of MgO with GGBS can reduce the strength slightly when cured under elevated CO₂ conditions as the MgO used within these mixes

was immediately carbonated and therefore was not available to activate the GGBS. Nevertheless, owing to its lower costs than MgO, substantial cost savings can be achieved by incorporating GGBS up to a certain extent within formulations subjected to natural curing conditions during which MgO is available to act as an activator.

(iii) Talc: As the crystal structure of talc contains brucite in between silica sheets, it has the potential to enhance the hydration and the subsequent carbonation of MgO cement formulations. It was seen that replacing 20% of MgO with talc did not cause any reductions in strength and maintained the same w/c ratio as the control mix, highlighting that talc can partially replace MgO without hindering the mechanical performance. This can also present environmental and economic advantages due to the common occurrence of magnesium silicates around the globe with lower production energy requirements and lower market values.

(iv) Serpentine: The carbonation of serpentine under high CO₂ pressures traps CO₂ as environmentally stable solid carbonates such as magnesite. The SC values of MgO (0.60) and serpentine (0.56) are very similar, indicating their compatibility in terms of maintaining the overall water content of the compositions generated. The use of serpentine at two different replacement ratios of 20% and 50% resulted in similar strengths as the control mix. Unlike other additives, strength of mixes increased with higher serpentine content, defining serpentine as one of the most feasible substitutes of MgO. Considering the high stability and low reaction potential of serpentine under the curing conditions presented in this study, the strength retention was attributed to the lower water contents of these mixes and the domination of nesquehonite as the main carbonation product. The monolithic nature of this particular HMC leads to higher bonding strengths than the other HMCs commonly observed within the MgO-CO₂-H₂O system.

An abundant formation of rosette-like hydromagnesite/dypingite, which formed well-ramified networks of crystals with a very effective binding ability, was observed after the accelerated carbonation of most mixes. Dense formation of monolithic networks of elongated nesquehonite crystals led to the high

strengths obtained by mixes containing serpentine and talc. Natural curing mostly resulted in a network of individually fused brucite particles, denoting incomplete carbonation as expected under low CO₂ concentrations. The quantification results obtained by each three methods were comparable: 100% carbonation was observed in the case of mixes with talc and serpentine, whereas those containing brucite and GGBS carbonated less. The degree of hydration varied from 70 to 100% amongst all mixes subjected to accelerated carbonation conditions, followed by full carbonation in most cases. The high extent of carbonation in all mixes was supported by the prominent peaks of different HMCs obtained by XRD analysis, including hydromagnesite, dypingite and nesquehonite. Peaks of MgO corresponding to incomplete hydration were also present, necessitating further comprehension of the constraint mechanism applied by brucite layers on the surface of magnesia and the imposed resistance that limits the further continuation of the hydration and the subsequent carbonation processes.

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