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Comparison of the environmental impacts of reactive magnesia and calcined dolomite and their performance under different curing conditions

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Abstract

This study presented a comparison of two binder systems composed of reactive magnesite cement (RMC) and calcined dolomite (D800), which were produced via the calcination of magnesite and dolomite at 800°C, respectively. The environmental impacts of the production of both binders were supported with an investigation of their strength and microstructural development in concrete samples subjected to different curing conditions. The lower energy and CO₂ emissions associated with D800 production led to reduced damage on human health and ecosystem in comparison to RMC production. The mechanical performance of both binder systems depended on their mix composition and curing conditions. Both benefited from the use of high humidity (90%), whereas elevated temperatures (60°C) presented an advantage only in RMC samples. The combination of high humidity and temperature enabled increased MgO dissolution and enhanced hydration/carbonation in RMC samples, thereby leading to higher strengths. D800 samples revealed lower strengths due to their lower initial MgO contents and initial porosities. Results of this study indicated the importance of customized curing conditions depending on the mix design and binder component.

Keywords: Reactive MgO; Dolomite; Humidity; Temperature; Microstructure; X-ray techniques; Environmental impact

Introduction

Mineral carbonation involves the sequestration of CO₂ as stable carbonates, such as calcite (CaCO₃), magnesite (MgCO₃) and dolomite (CaMg(CO₃)₂). The use of carbonation curing in cement-based mixes can offset CO₂ emissions released during cement production and increase strength, which is more obvious under accelerated conditions (Bertos et al. 2004; Pade and Guimaraes 2007). Differing from Portland cement (PC), reactive magnesia (MgO) cement (RMC)-based mixes have gained attention due to their lower production temperatures (i.e. 700-1000 vs. 1450 °C for PC) and ability to gain strength via carbonation. This carbonation process leads to the formation of carbonate phases such as nesquehonite (MgCO₃·3H₂O) and hydromagnesite (4MgCO₃·Mg(OH)₂·4H₂O), which contribute to strength development by establishing a dense carbonate network that enables a reduction in sample porosity (Dung and Unluer 2016; Liska and Al-Tabbaa 2009; Ruan and Unluer 2017a). When their ability to sequester CO₂ in the form of stable carbonates and/or incorporation of other by-products within the mix design is taken into account, RMC formulations can present an advantage in terms of their lower environmental impacts than corresponding PC formulations (Mo et al. 2016; Ruan and Unluer 2016; Ruan and Unluer 2017c).

Some of the main factors influencing the strength development of RMC mixes is the extent of hydration (i.e. conversion of MgO into Mg(OH)₂, brucite) and subsequent carbonation reaction, as well as the morphology of the phases that form at the end of the curing process (Ruan and Unluer 2017b; Unluer and Al-Tabbaa 2014). RMC is obtained through the calcination of Mg-bearing carbonates such as magnesite and dolomite at ~700-1000 °C (Jin and Al-Tabbaa 2014). Dolomite, composed of Ca- and Mg-carbonates, presents a suitable source for RMC production due to its relatively low cost and abundance (Warren 2000). Similar to other Mg-based carbonate phases, the thermal decomposition of dolomite can take place in two stages: (i) decomposition into MgO and calcite (CaCO₃) at around 700-750 °C, as shown in Equation 1; and (ii) decomposition of calcite at > 700 °C, as shown in Equation 2 (Caceres and Attiogbe 1997; Maitra et al. 2005; Ruan et al. 2017; Sasaki et al. 2013).

69
70 One way of extracting Mg from dolomite is through the Pidgeon process, which
71 involves the initial calcination of the raw material (i.e. dolomite), followed by the
72 introduction of ferrosilicon for the separation of Mg and Ca, which are the main phases
73 obtained when dolomite is calcined (Ramakrishnan and Koltun 2004). Dolomite can
74 also be used as a starting material in the production of magnesium oxychloride cement,
75 which also leads to the production of high-purity CaCO_3 and CO_2 (Altiner and Yildirim
76 2017a; Altiner and Yildirim 2017c). Other studies on the use of dolomite have reported
77 the properties of an alkali-activated cement system involving a mix of dolomite and
78 bentonite subjected to calcination under high temperatures (~1100-1200 °C) (Peng et
79 al. 2017). Another study (Szybalski and Nocuń-Wczelik 2015) investigated the role of
80 dolomite on the hydration of cement, where dolomite was added as an active ingredient
81 or as a cement replacement at low dosages. Half-burnt dolomite, composed of MgO
82 and CaCO_3 , has also been used as a supplementary cementitious material (SCM) to
83 partially replace PC. The replacement of up to 20-25% PC by half-burnt dolomite was
84 reported to retain compressive strength at 28 days, while the maximum strength gain
85 was observed at a replacement level of around 10-15%. Within these mixes, the
86 particle size distribution and accessibility of MgO to water greatly affected the reactivity
87 of half-burnt dolomite used as a SCM (Jauffret and Glasser 2016). Other than its use
88 as an additive within the binder content, raw dolomite extracted as a natural resource
89 can also be used as a coarse aggregate within concrete mixes (Prokopski and
90 Halbiniak 2000).

91
92 There are several studies that investigated the influence of key environmental factors
93 such as temperature and relative humidity (RH) on the performance of traditional PC-
94 based concrete samples. The findings reported by these studies (Bai et al. 2002; Kim
95 et al. 1998) indicated that elevated curing temperatures (40 °C) enabled high early
96 strength gain, while resulting in lower long-term strengths due to the uneven
97 distribution of hydrate phases. Furthermore, concrete samples cured under high
98 humidity levels (100%) were reported to achieve significantly higher strengths than
99 those cured under lower humidity environments due to the lower levels of shrinkage
100 and deformation in the former case. On the other hand, carbonated RMC-based
101 concrete samples cured under various RH values ranging between 55% and 98% did
102 not indicate a linear trend in terms of their strength development. Within these samples,

those cured under a RH of 78% led to the highest strengths due to the sufficient presence of water that enabled the continuation of the carbonation reaction, while not reducing the diffusion rate of CO₂ within the pore system (Unluer and Al-Tabbaa 2014). Another study (Leemann and Moro 2017) investigating the effect of RH and CO₂ concentration on the carbonation of concrete mixes containing different cement types showed that under a CO₂ concentration of 4%, an increase in RH from 57% to 70-80% inhibited carbonation as more pores were filled with water under high humidities. On the other hand, when the RH was < 70%, carbonation resistance was mainly determined by the CO₂ buffer capacity.

While its use as an additive or aggregate component has been reported, the role of dolomite as a binder component has not been fully explored until now. In addition to its performance under different curing conditions, the environmental impacts of dolomite-based binders remain to be studied. In line with these gaps in the literature, the main goal of this study is to assess the environmental impacts of calcined dolomite, evaluate its performance as a binder in concrete samples subjected to different curing conditions and provide a comparison with RMC-based samples. To enable this, the environmental implications of these binders were supported with the investigation of the strength and microstructural development of calcined dolomite and RMC-based concrete samples cured under different temperature and RH conditions. The obtained results were aimed to shed light on the potential of each binder system under different conditions and pave the way for the optimization of conditions that will lead to maximum performance for Mg-based systems.

Materials and Methodology

Materials

RMC was obtained from Richard Baker Harrison (UK). Raw dolomite, obtained from International Scientific (Singapore), was calcined at 700, 800 and 900 °C (i.e. to determine the desired calcination temperature) for 3 hours and ground at a speed of 300 revolutions/minute for 10 minutes to achieve a similar particle size distribution as RMC. The equipment used for this purpose was a Planetary Mono Mill Pulverisette 6 classic line, equipped with stainless steel grinding balls. The particle size distribution of

RMC and D800 is shown in Fig. 1. The chemical compositions of RMC (i.e. provided by the supplier) and calcined dolomite (i.e. generated by XRD-based phase quantification performed via Rietveld refinement software TOPAS 5.0, whose details are provided in the “Reaction mechanisms, mechanical performance and microstructural analysis” Section) are provided in Table 1. Natural siliceous coarse aggregates, supplied by Buildmate (Singapore) with a particle size of 4.7-9.5 mm, were used to form the aggregate profile in the concrete mixes.

Environmental assessment

The environmental impacts associated with the production of the two types of binder used in this study (i.e. RMC and calcined dolomite) were assessed by life cycle assessment (LCA), performed according to ISO 14040 (ISO14040 2006). The background data used in the LCA were obtained from the Ecoinvent database developed by the Swiss Centre for Life Cycle Inventories (Ecoinvent 2014) and the ETH-ESU database, provided by Eidgenössische Technische Hochschule (ETH-ESU 1996).

Amongst all the processes involved in the production of both binders, the calcination process is the most energy intensive. Therefore, the system boundary used in this study mainly focused on the calcination step used in the production of RMC and calcined dolomite, as shown in Fig. 2. The functional unit of assessment used was 1 tonne of RMC and calcined dolomite. In this LCA study, Eco-indicator 99 was used to select various indicators for the quantification of the environmental burdens of the production processes across a wide range of categories. The damage-oriented Eco-indicator 99 was chosen as it provides an assessment of the environmental aspects of different product systems based on conceptual models and describes various environmental impacts ranging from climate change to ecotoxicity. Life cycle impact assessment for 12 midpoint impact categories including climate change was conducted and the endpoint results were generated according to Eco-indicator 99, which involved the normalization of the final output in the interpretation of the LCA results (Goedkoop et al. 2010). The detailed heat and energy calculations, as well as the power consumption associated with each process are listed in the Appendix section.

Sample preparation

Once the calcination temperature to be used during the production of calcined dolomite was determined, concrete samples, whose binder component included calcined dolomite (D) or RMC (M) were prepared to compare the performance and microstructural development of each binder under different curing conditions. The w/b of each composition was determined according to the standard consistency of RMC and calcined dolomite, which was measured as 0.60 and 0.29 according to BS EN 196-3 (BSI 2016), respectively. This led to the preparation of concrete samples with similar workabilities, containing 40% binder and 60% coarse aggregates. The mix compositions of all samples are listed in Table 2.

A Hobart HL200 Legacy Planetary mixer was used with a stirring speed of 59 RPM during mixing. The dry powders were mixed first, followed by the gradual addition of water into the dry mix. The formed paste was mixed for around 5 minutes before the aggregates were added, after which the mixing process continued for another 5 minutes. The prepared mix was then cast into 50×50×50 mm³ cubic molds, consolidated by a vibrating table and trowel finished. The molds were placed in a plastic box kept at 28±2 °C for 24 hours, accompanied with silica gel to remove the surface moisture of samples in preparation for the subsequent carbonation process (Mo and Panesar 2013). After 24 hours, all samples were demolded and placed in an environmental chamber under three different conditions for up to 14 days: (i) 50% RH, 30 °C, 10% CO₂ (R50T30C10), (ii) 90% RH, 30 °C, 10% CO₂ (R90T30C10), and (iii) 90% RH, 60 °C, 10% CO₂ (R90T60C10). The details of the curing conditions used in this study are listed in Table 3.

Reaction mechanisms, mechanical performance and microstructural analysis

The hydration behavior of each mixture was studied in terms of their heat flow and cumulative heat measured by an I-Cal 8000 high precision isothermal calorimeter at 30 and 60 °C in accordance with ASTM C1702-17 (ASTM 2017). To prepare the samples, 20 g of each binder was mixed with pre-heated distilled water at corresponding w/b

ratios. The time spent on the mixing and loading processes was minimized to less than a minute to fully observe the heat evolution of each system.

The mechanical performance of the prepared concrete samples was assessed via compressive strength testing at 1, 7 and 14 days at a loading rate of 50 kN/min. 3 samples were tested to obtain each data point and corresponding standard deviation. The compressive strength results were correlated with the initial (i.e. before the carbonation process started) porosities of each sample. The initial porosity values were calculated according to Equation 3, where m_{sat} is the sample mass saturated in water, m_{dry} is the sample mass dried at 70 °C to constant mass and V is the sample volume.

$$P = (m_{sat} - m_{dry}) / V \times 100\% \quad (3)$$

Once the curing process was completed, surfaces of selected samples were polished with sand paper and observed under an OPTEM Zoom 70XL microscope. The images were captured by Nikon DS-Fi2 high resolution camera equipped with NIS Elements (Nikon) software at a magnification of 84x. Samples extracted from the cubes crushed during compressive strength test were stored in acetone for at least 3 days to stop hydration in preparation for microstructural analysis. Thermogravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscopy (SEM) combined with energy dispersive x-ray (EDX) for elemental analysis were used to investigate the extent of hydration and carbonation and morphology of the formed phases. TGA was conducted on a Perkin Elmer TGA 4000 equipment from 30 to 900 °C with a heating rate of 10 °C/min under nitrogen flow. For XRD analysis, powders were extracted from the paste sections of selected samples to ensure no aggregates were involved. The obtained powders were then sieved and vacuum-dried for 24 hours before being analyzed with a Philips PW1800 spectrometer using Cu K α radiation (40 kV, 40 mA) with a scanning rate of 2° 2 θ /step between 5-80° 2 θ . Phase quantifications were performed via Rietveld refinement software TOPAS 5.0 with fundamental parameter approach. Since the total mass of solids does not stay constant during the hydration and carbonation of MgO, the back calculation of Rietveld results was also conducted by normalizing the initially obtained quantitative results to a common basis (e.g. ignited binder mass), as shown in Equation 4 (Scrivener et al. 2016).

$$W_{(j, rescaled)} = W_{(j, Rietveld)} / [(1 - H_2O_{bound} - CO_{2bound})(1 + (w/c))] \quad (4)$$

Microstructural observation of representative samples was performed by SEM (JSM-7600F operated at an acceleration voltage of 5 kV and working distance of 8 mm) and EDX (Oxford X-Max 80 mm² operated at an acceleration voltage of 15 kV and working distance of 15 mm). Samples that were previously stored in acetone and vacuum dried were attached to sample holders by carbon tapes and gold-coated before SEM-EDX.

Results and Discussion

Selection of calcination temperature for dolomite

Before the comparison of RMC and calcined dolomite-based concrete samples, dolomite was calcined at three different calcination temperatures to determine the optimum conditions that led to the production of dolomite with the highest MgO content, while minimizing the decomposition of calcite (i.e. CaO content). In addition to the chemical composition data provided in Table 1, preliminary trials were conducted by preparing concrete samples, whose binder composition was composed of equal amounts of D700, D800 and D900 produced under calcination temperatures of 700, 800 and 900 °C, respectively. These samples were cured for 14 days under ambient RH and temperature, while the CO₂ concentration was maintained at 10%. The performance of each calcined dolomite sample was assessed via the compressive strengths of concrete samples, as shown on Fig. 3.

Samples calcined at 800 °C (D800) led to the highest strengths amongst all samples, followed by those calcined at 700 °C (D700) and 900 °C (D900). The highest strengths obtained by D800 samples was associated with their low CaO contents, because calcite was not decomposed at temperatures $\leq$ 800 °C, as shown in Table 1. Alternatively, increasing the calcination temperature to 900 °C in D900 led to the simultaneous presence of MgO and CaO, which slowed down the hydration of MgO. This reduction in the hydration of MgO was associated with the common ion effect, which involves the physical interaction between two different salts or minerals with a common ion (e.g. OH⁻ ion within Ca(OH)₂ and Mg(OH)₂) and states that the solubility of the originally less soluble one will decrease even further in the presence of the other (Atkins 2013). In this case, as the solubility of Mg(OH)₂ is much lower than that of

Ca(OH)₂ (i.e. $\sim 1.5 \times 10^{-4}$ vs. $\sim 2.4 \times 10^{-2}$ mol/L at 298 K), the hydration rate of MgO can reduce in the presence of Ca(OH)₂ (Liska 2010), thereby lowering the overall hydration and carbonation degrees and the associated strength gain of D900. Furthermore, increasing the calcination temperature is also known to cause sintering, which increases the mean particle size and decreases the reactivity of MgO (Altiner and Yildirim 2017b; Itatani K et al. 2002). Another study (Mo et al. 2010) reported that MgO samples produced under high calcination temperatures have less porous structures and larger crystal sizes, leading to slower hydration rates. On the other hand, utilization of calcination temperatures as low as 700 °C in D700 resulted in the incomplete decomposition of magnesite, reducing the reactive MgO content of the final binder. The lower MgO content of D700 limited its strength development, identifying 800 °C as the ideal temperature for the calcination of dolomite. Therefore, D800 was chosen as the calcined dolomite-based binder and was compared with RMC in terms of its environmental assessment, mechanical performance and microstructural development.

Environmental assessment

Amongst all the steps that lead to the final product of RMC or calcined dolomite, the calcination process, which involves the decomposition of carbonate phases (i.e. magnesite or dolomite), requires the highest energy and results in the highest amount of CO₂ emissions (An and Xue 2017; Li et al. 2015; Ruan and Unluer 2016). In line with its chemical composition presented earlier in Table 1, the production of D800 necessitated the decomposition of only magnesite within dolomite. Meanwhile, the calcite component within the parent material dolomite remained intact, as revealed by the limited CaO content of 0.3% within D800, which was composed of $\sim 28\%$ MgO and $\sim 72\%$ calcite. Similarly, the production of RMC also involved the decomposition of magnesite into MgO, which was assumed to take place at 800 °C. Therefore, the total heat required during the production both binders (i.e. RMC and D800), was mainly associated with the process of calcination, during which magnesite/dolomite decomposed into MgO at 800 °C. The main energy source for both processes was assumed to be coal-based as coal is accountable for approximately 70% of China's primary energy supply (Chai and Zhang 2010), the main worldwide producer of RMC.

Then inventory for the production of 1 tonne of RMC and D800 is shown in Table 4. When the two binders were compared, the production of D800 involved lower amounts of raw materials as well as energy and CO₂ emissions than the production of an equivalent amount of RMC. These lower outputs (i.e. energy and CO₂ emissions) associated with D800 production corresponded to reduced impacts on human health and ecosystem quality in comparison to RMC production, as shown in Fig. 4 (a). Albeit more pronounced in the human health category, the reduced impact of D800 was attributed to its lower raw materials (i.e. MgO) content, as well as the lower amount of coal used during its production. Regarding the damage to resources, RMC and D800 presented similar scores even though their energy consumption was not the same, which could be due to the extraction of different raw materials (i.e. magnesite/dolomite). Unlike RMC, the production of D800 did not require the complete decomposition of dolomite, which translated into reduced environmental impacts. A similar trend was also observed in the comparison of the global warming potential (GWP) of each binder shown in Fig. 4 (b), which was reflected in terms of the total amount of CO₂-eq released during production. Collectively, these results indicate that calcined dolomite can be considered as a sustainable alternative source for the production of MgO-based binders that are more environmentally-friendly than RMC produced through the dry route (i.e. involving the calcination of magnesite).

Isothermal calorimetry

Before subjecting each sample to carbonation, their hydration mechanisms under different temperatures were studied via isothermal calorimetry. The heat flow and cumulative heat data of RMC and D800 pastes generated during the first 72 hours of hydration under 30 and 60 °C are indicated in Fig. 5 (a) and (b), respectively. Under both temperatures, RMC samples achieved a high initial heat flow peak due to the higher availability of MgO in comparison to D800 samples. The larger specific surface area of RMC particles associated with their smaller sizes than D800 could have contributed to the higher initial peaks demonstrated. The intensity of the initial peak reduced with the use of dolomite in D800. The lower heat flows of samples containing D800 were partially attributed to the reduction of the hydration degree due to the common ion effect associated with the presence of CaO along with MgO. The lower peak intensities and cumulative heats were also an outcome of the lower initial MgO

(i.e. the main binder phase) and water contents in D800 samples. This could explain the highest heat flow peak as well as the largest amount of cumulative heat exhibited by RMC samples, which demonstrated a higher initial and overall hydration degree than D800 samples.

An increase in the temperature from 30 to 60 °C led to an obvious increase in the initial hydration peak of both binders, which was an indication of a higher rate of hydration under the elevated temperature. A similar trend was observed in the initial cumulative heat results of RMC samples recorded during the first ~60 hours of hydration. However, the influence of high temperature was less obvious at longer durations (> 60 hours), at which both temperatures led to similar cumulative heats. These findings were in line with those of PC-based mixes, where an increase in the initial hydration rate observed under elevated temperatures was reported to be accompanied with a lower ultimate heat release (Kjellsen and Detwiler 1992). Unlike RMC samples, the hydration of D800 samples did not benefit from the elevated temperature of 60 °C, revealed by their lower cumulative heat when compared to D800 samples analyzed under 30 °C. The lower amount of heat observed in D800 samples under the elevated temperature could be associated with the lower availability of water within this mix design, which could have limited the hydration process under 60 °C. Overall, other than the properties of the binders themselves, their chemical composition and temperature were identified as the main parameters controlling the extent of the hydration reaction.

Compressive strength

After assessing the hydration mechanisms via isothermal calorimetry, the extent of carbonation and associated mechanical performance within each sample were studied under different RH (50% and 90%) and temperatures (30 °C and 60 °C), while the CO₂ concentration was kept constant at 10%. The compressive strength development of samples containing RMC and D800 subjected to curing under different conditions are shown in Fig. 6 (a). Differences in the mechanical performance of each sample were associated with variations in curing conditions, binder component and initial water content. The changes in these parameters led to different initial porosity values, which were recorded as ~30% and 15% for RMC- and D800-based concrete samples, respectively. These different porosity values were justified by the need to prepare

samples with the same workability level, which necessitated the use of different water contents for each binder system. Water content has a twofold role in strength development. It is needed for the continuation of hydration and carbonation, while it also determines the initial porosity that influences the penetration of CO₂ within samples and hence the final carbonation degree (Mo and Panesar 2012; Mo and Panesar 2013; Unluer and Al-Tabbaa 2014).

While no significant differences were observed in the early (1-day) strengths of all samples, the higher initial porosities of RMC samples may have enabled the diffusion of a larger amount of CO₂ within the sample pore system, thereby increasing their overall strength obtained after 14 days of curing. The main strength development of all samples took place during the first 7 days due to the formation of a dense carbonate network. Although contributing to strength gain, the reduction in porosity associated with carbonate formation during the first 7 days may have inhibited the penetration of further CO₂ into the pore system in the later ages, which was in line with the findings of previous studies (Harada et al. 2015; Ruan and Unluer 2017b; Ruan and Unluer 2017c).

In addition to the initial mix design, the strength results shown in Fig. 6 (a) indicated the significant influence curing conditions played in the performance of each sample. The combination of high temperature (60 °C) and humidity (90%) revealed the highest strengths of 43 and 51 MPa in RMC samples at 7 and 14 days, respectively. The reduction of temperature to 30 °C under 90% RH led to a 35% reduction in the strength of M to ~33 MPa. A further reduction in the strength of RMC samples to ~20 MPa was observed under 30 °C and 50% RH. These trends indicate the necessity of high humidity and temperature in enhancing the dissolution of MgO, precipitation of brucite and its subsequent carbonation via the accelerated diffusion of CO₂.

A different scenario was observed in D800 samples, which demonstrated their best performance (28 MPa at 14 days) under 30 °C and 90% RH. While D800 samples benefited from curing under high RH levels, a reduction in strength was observed when the temperature was raised to 60 °C. This was associated with the lack of reactive phase (MgO) and formation of micro-cracks under elevated temperatures due to the lower initial water content of D800 samples. These findings were in line with the isothermal calorimetry measurements shown in Fig. 5 (b), which indicated a lower

cumulative energy during the hydration of D800 under 60 °C when compared to 30 °C. The limited hydration capabilities of these samples also led to reduced carbonation and associated strength development. Furthermore, microscopic images of the surfaces of RMC and D800 samples cured under 60 °C and 90% RH revealed the formation of cracks in D800 samples, as shown in Fig. 7. Therefore, the inferior performance of D800 samples could be associated with their lower hydration, which inhibited the subsequent carbonation reaction; as well as the formation of cracks under elevated temperatures.

Out of the two binder systems, the improved performance of RMC samples was linked with their higher degree of hydration and carbonation enabled by the presence of sufficient reactive phase (MgO) and water; and their high initial porosity, which facilitated the diffusion of CO₂ within the pore system. To consider the effect of MgO content within each binder in the comparison of sample performance, the 14-day compressive strengths of all samples per unit of MgO content are shown in Fig. 6 (b). Differing from the previous observation, D800 samples cured under 30 °C and 90% RH outperformed all RMC-based samples due to their low MgO content. Similarly, D800 samples cured under 60 °C and 90% RH revealed a comparable performance as the RMC samples cured under the same conditions, indicating the possibility of using calcined dolomite as a binder in concrete formulations.

XRD and TGA

The XRD patterns of selected carbonated RMC and D800 samples cured for 14 days are shown in Fig. 8. While the presence of MgO and brucite dominated the sample composition, hydromagnesite and nesquehonite were identified as the main carbonate phases in RMC samples. The ignited binder mass extracted from the TGA curves of the same RMC and D800 samples cured for 14 days, as shown in Fig. 9, were used to normalize the phase quantification results obtained from Rietveld refinement, as described in (Scrivener et al. 2016). The initial (i.e. before normalization) and the normalized quantities of major phases in each sample after 14 days of curing are listed in Tables 5 and 6, respectively. An obvious reduction in the amount of MgO, accompanied with an increase in brucite and carbonates was observed under the simultaneous increase of temperature (60 °C) and humidity (90%). These were in line

with the strength results, where an increase in strength was observed under elevated temperature and humidity conditions. Along with small amounts of MgO, brucite and hydromagnesite, calcite that remained undecomposed during the calcination of dolomite was observed in D800 samples.

A direct relationship could be established between the amount of unhydrated MgO/carbonates and strength development. An obvious reduction in the residual MgO content was observed at higher humidity and temperatures, which led to a simultaneous increase in the amount carbonates. Amongst RMC samples, lower residual MgO and higher carbonate contents of samples cured under 60 °C and 90% RH could explain their improved mechanical performance, enabled by the higher degree of MgO utilization. The correlation between curing conditions and phase formations could explain the strength development of each formulation (Mo and Panesar 2012; Mo and Panesar 2013; Unluer and Al-Tabbaa 2014). The reduction of nesquehonite and corresponding increase of hydromagnesite at 60 °C could be due to the higher stability of the latter at elevated temperatures (Davies and Bubela 1973). Unlike RMC samples, D800 samples revealed smaller amounts of residual MgO and brucite. This was an indication of the higher conversion of MgO into brucite and carbonates within D800 samples. These differences in the conversion degrees could be associated with the lower initial MgO content of D800 (~28%) than that of RMC (~94%), as shown earlier in Table 1. In spite of their higher conversion degrees, the limited initial MgO content of D800 samples presented a barrier in their strength development. Curing under high humidity (90%) and ambient temperatures (30 °C) revealed the highest hydromagnesite content amongst all D800 samples, which was in line with the strength results. Similarly, the lower carbonate contents of D800 samples cured under 30 °C and 50% RH corresponded well with their low strengths, highlighting the direct link between curing conditions and the extent of carbonation as well as the associated mechanical performance.

Microstructural analysis

The formation and morphology of phases within carbonated RMC and D800 samples that revealed the highest and lowest strengths were illustrated with SEM images shown in Fig. 10. Within both formulations, the formation of rosette-like hydromagnesite was

visible in those subjected to high humidity (90%), which could explain their improved strength development. Elemental analysis obtained via EDX not only proved the formation of Mg-carbonates (e.g. hydromagnesite) in both compositions, but also indicated the presence of Ca in D800 samples, which was associated with the initial composition of the parent material, dolomite. Microstructural densification enabled by the formation of a strong carbonate network within these samples corresponded well with their performance. Alternatively, the combination of lower humidity (50%) and temperature (30 °C) revealed the widespread presence of uncarbonated brucite and MgO, leading to porous structures that accounted for an inferior mechanical performance.

Conclusions

This study involved the use of two magnesium-based binders, obtained via the calcination of magnesite (RMC) and dolomite (D800), in concrete formulations. The obtained results presented a comparison of the environmental impacts and performance of these binders by investigating their production processes as well as strength and microstructural development in concrete samples under different curing conditions. A calcination temperature of 800 °C was determined to be ideal for the production of the dolomite-based binder (D800), which led to higher strength results and MgO contents than those obtained under lower (700 °C) and higher (900 °C) calcination temperatures. When compared to RMC produced through the calcination of magnesite under the same temperature (800 °C), the production of D800 revealed lower environmental impacts as well as reduced damage to human health, which was associated with lower emissions of CO₂ and use of energy during this process.

In terms of their mechanical performance, the main factors controlling the strength development of each binder system were identified as the binder component, initial water content and curing conditions. The higher content of MgO available for hydration and carbonation, and the larger initial porosity enabling increased CO₂ diffusion within RMC samples led to higher strengths than those of D800 samples. The use of higher humidity levels favored the strength development of both binder systems through increased brucite formation. Increased temperatures led to a higher dissolution of MgO and its use in subsequent hydration and carbonation reactions in RMC samples,

whereas it had adverse effects in the strength of D800 samples containing lower initial amounts of MgO and water. A comparison of the 14-day compressive strength of all samples per unit of MgO content revealed that D800 samples cured under 30 °C and 90% RH outperformed all RMC-based samples due to their low MgO contents. Similarly, D800 samples cured under 60 °C and 90% RH revealed a comparable performance as the RMC samples cured under the same conditions, indicating the possibility of using calcined dolomite as a binder in concrete formulations. The results of this study demonstrated that the optimum curing conditions are different for each binder system and must be customized accordingly to facilitate hydration and carbonation and achieve maximum performance within each formulation.

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References

- Altiner M, Yildirim M. (2017a). "Influence of filler on the properties of magnesium oxychloride cement prepared from dolomite." *Emerging Materials Research*, 1-5.
- Altiner M, Yildirim M. (2017b). "Preparation of periclase (MgO) nanoparticles from dolomite by pyrohydrolysis – calcination processes." *Asia-Pacific Journal of Chemical Engineering*.
- Altiner M, Yildirim M. (2017c). "Study of using dolomite as starting material resource to produce magnesium oxychloride cement." *Journal of Advanced Concrete Technology*, 15(6), 269-277.
- An J, Xue X. (2017). "Life-cycle carbon footprint analysis of magnesia products." *Resources, Conservation and Recycling*, 119, 4-11.
- ASTM (2017). "C1702-17, Standard test method for measurement of heat of hydration of hydraulic cementitious materials using isothermal conduction calorimetry." *ASTM Committee C01, West Conshohocken, PA 19428-2959, United States*.
- Atkins PW (2013). *The elements of physical chemistry*, 6th Edition, Oxford University Press Oxford United Kingdom.

557 Bai J, Wild S, Sabir B. (2002). "Sorptivity and strength of air-cured and water-cured
 558 PC–PFA–MK concrete and the influence of binder composition on carbonation depth."
 559 *Cement and Concrete Research*, 32(11), 1813-1821.
 560 Bertos MF, Simons S, Hills C, Carey P. (2004). "A review of accelerated carbonation
 561 technology in the treatment of cement-based materials and sequestration of CO₂."
 562 *Journal of Hazardous Materials*, 112(3), 193-205.
 563 BSI (2016). "BS EN 196-3:2016, Methods of test cement. Determination of setting
 564 times and soundness." British Standards Institution, London, United Kingdom.
 565 Caceres PG, Attiogbe EK. (1997). "Thermal decomposition of dolomite and the
 566 extraction of its constituents." *Minerals Engineering*, 10(10), 1165-1176.
 567 Chai Q, Zhang X. (2010). "Technologies and policies for the transition to a sustainable
 568 energy system in China." *Energy*, 35(10), 3995-4002.
 569 Davies PJ, Bubela B. (1973). "The transformation of nesquehonite into
 570 hydromagnesite." *Chemical Geology*, 12(4), 289-300.
 571 Dung N, Unluer C. (2016). "Improving the performance of reactive MgO cement-based
 572 concrete mixes." *Construction and Building Materials*, 126, 747-758.
 573 Ecoinvent. (2014). "The life cycle inventory data. Swiss Centre for Life Cycle
 574 Inventories, Duebendorf, Switzerland."
 575 ENS www.euronuclear.org/info/encyclopedia/coalequivalent.htm, European Nuclear
 576 Society, Avenue des Arts 56, 1000 Brussels, Belgium, August, 2012.
 577 ETH-ESU. (1996). "Ökoinventare von Energiesystemen. ESU Group, ETH Technical
 578 University of Zürich."
 579 Goedkoop M, Schryver A, Oele M, Durksz S, de Roest D (2010). "Introduction to LCA
 580 with SimaPro 7. Pré Consultants."
 581 Harada T, Simeon F, Hamad EZ, Hatton TA. (2015). "Alkali metal nitrate-promoted
 582 high-capacity MgO adsorbents for regenerable CO₂ capture at moderate
 583 temperatures." *Chemistry of Materials*, 27(6), 1943-1949.
 584 ISO14040 (2006). "Environmental management: life cycle assessment—principles and
 585 frameworkment. International Standards Organization, p. 23." Geneva, Switzerland.
 586 Itatani K, Shiobara M, FS H. (2002). "Effect of bimodal particle size distribution on the
 587 sintering of magnesium oxide powder." *The Society of Inorganic Materials, Japan*, 9,
 588 498-504.
 589 Jauffret G, Glasser FP. (2016). "Thermally activated dolomite as pozzolanic addition to
 590 Portland cement." *Advances in Cement Research*, 28(6), 378-388.

591 Jin F, Al-Tabbaa A. (2014). "Characterisation of different commercial reactive
592 magnesia." *Advances in Cement Research*, 26(2), 101-113.

593 Kim J-K, Moon Y-H, Eo S-H. (1998). "Compressive strength development of concrete
594 with different curing time and temperature." *Cement and Concrete Research*, 28(12),
595 1761-1773.

596 Kjellsen KO, Detwiler RJ. (1992). "Reaction kinetics of Portland cement mortars
597 hydrated at different temperatures." *Cement and Concrete Research*, 22(1), 112-120.

598 Li J, Zhang Y, Shao S, Zhang S. (2015). "Comparative life cycle assessment of
599 conventional and new fused magnesia production." *Journal of Cleaner Production*, 91,
600 170-179.

601 Liska M (2010). "Properties and applications of reactive magnesia cements in porous
602 blocks." University of Cambridge.

603 Liska M, Al-Tabbaa A. (2009). "Ultra-green construction: reactive magnesia masonry
604 products." *Proceedings of the ICE-Waste and Resource Management*, 162(4), 185-196.

605 Maitra S, Choudhury A, Das HS, Pramanik MJ. (2005). "Effect of compaction on the
606 kinetics of thermal decomposition of dolomite under non-isothermal condition." *Journal*
607 *of Materials Science*(18), 4749-4751.

608 Mo L, Deng M, Tang M. (2010). "Effects of calcination condition on expansion property
609 of MgO-type expansive agent used in cement-based materials." *Cement and Concrete*
610 *Research*, 40(3), 437-446.

611 Mo L, Panesar DK. (2012). "Effects of accelerated carbonation on the microstructure
612 of Portland cement pastes containing reactive MgO." *Cement and Concrete Research*,
613 42(6), 769-777.

614 Mo L, Panesar DK. (2013). "Accelerated carbonation—a potential approach to
615 sequester CO₂ in cement paste containing slag and reactive MgO." *Cement and*
616 *Concrete Composites*, 43, 69-77.

617 Mo L, Zhang F, Panesar DK, Deng M. (2016). "Development of low-carbon
618 cementitious materials via carbonating Portland cement–fly ash–magnesia blends
619 under various curing scenarios: a comparative study." *Journal of Cleaner Production*
620 (<http://dx.doi.org/10.1016/j.jclepro.2016.01.066>).

621 Pade C, Guimaraes M. (2007). "The CO₂ uptake of concrete in a 100 year
622 perspective." *Cement and Concrete Research*, 37(9), 1348-1356.

623 Peng MX, Wang ZH, Xiao QG, Song F, Xie W, Yu LC, Huang HW, Yi SJ. (2017).
624 "Effects of alkali on one-part alkali-activated cement synthesized by calcining bentonite
625 with dolomite and Na₂CO₃." *Applied Clay Science*, 139, 64-71.

- Prokopski G, Halbiniak J. (2000). "Interfacial transition zone in cementitious materials." *Cement and Concrete Research*, 30(4), 579-583.
- Ramakrishnan S, Koltun P. (2004). "Global warming impact of the magnesium produced in China using the Pidgeon process." *Resources, Conservation and Recycling*, 42(1), 49-64.
- Ruan S, Liu J, Yang E-H, Unluer C. (2017). "Performance and microstructure of calcined dolomite and reactive magnesia-based concrete samples." *Journal of Materials in Civil Engineering*, 29(12), 04017236.
- Ruan S, Unluer C. (2016). "Comparative life cycle assessment of reactive MgO and Portland cement production." *Journal of Cleaner Production*, 137, 258-273.
- Ruan S, Unluer C. (2017a). "Effect of air entrainment on the performance of reactive MgO and PC mixes." *Construction and Building Materials*, 142, 221-232.
- Ruan S, Unluer C. (2017b). "Influence of mix design on the carbonation, mechanical properties and microstructure of reactive MgO cement-based concrete." *Cement and Concrete Composites*, 80, 104-114.
- Ruan S, Unluer C. (2017c). "Influence of supplementary cementitious materials on the performance and environmental impacts of reactive magnesia cement concrete." *Journal of Cleaner Production*, 159, 62-73.
- Sasaki K, Qiu X, Hosomomi Y, Moriyama S, Hirajima T. (2013). "Effect of natural dolomite calcination temperature on sorption of borate onto calcined products." *Microporous and Mesoporous Materials*, 171, 1-8.
- Scrivener K, Snellings R, Lothenbach B (2016). *A practical guide to microstructural analysis of cementitious materials*, Taylor & Francis Group, LLC.
- Szybilski M, Nocun-Wczelik W. (2015). "The effect of dolomite additive on cement hydration." *Procedia Engineering*, 108, 193-198.
- Unluer C, Al-Tabbaa A. (2014). "Enhancing the carbonation of MgO cement porous blocks through improved curing conditions." *Cement and Concrete Research*, 59, 55-65.
- Warren J. (2000). "Dolomite: occurrence, evolution and economically important associations." *Earth-Science Reviews*, 52(1), 1-81.

List of Tables

Table 1. Chemical compositions of RMC and calcined dolomite

Binder	Chemical composition (%)							
	MgO	CaO	CaCO ₃	CaMg(CO ₃)	SiO ₂	Fe ₂ O ₃	Na ₂ O	K ₂ O
RMC	94.1	1.6	-	-	0.3	0.7	1.3	0.5
D700	10.6	-	30.5	58.9	-	-	-	-
D800	27.6	0.3	71.7	0.4	-	-	-	-
D900	32.6	7.6	59.8	-	-	-	-	-

Table 2. Mix compositions used in this study

Sample	Binder (%)		Aggregates (%)	w/b
	RMC	Calcined dolomite		
M	40	0	60	0.60
D700	0	40	60	0.29
D800	0	40	60	0.29
D900	0	40	60	0.29

Table 3. Various curing conditions used in this study

Curing condition	RH (%)	Temperature (°C)	CO ₂ concentration (%)
R50T30C10	50	30	10
R90T30C10	90	30	10
R90T60C10	90	60	10

Table 4. Inventory for the production of 1 tonne of RMC and calcined dolomite (D800)

Binder	Raw material (type)	Amount of raw material (tonnes) ^a	Energy (coal, kg) ^b	CO ₂ emissions (tonne) ^a
RMC	Magnesite	2.1	151.1	1.1
D800	Dolomite	1.3	71.8	0.3

a: based on theoretical calculations in accordance with the chemical reactions

b: based on theoretical calculations, as shown in the Appendix

Table 5. Percentage quantities of the major phases within selected samples after 14 days of curing, obtained via Rietveld refinement (i.e. before normalization)

Sample	MgO	Brucite	Nesquehonite	Hydromagnesite	Calcite
M-R50T30C10	53.7	43.6	0.4	2.3	-
M-R90T30C10	30.5	37.7	6.6	25.2	-
M-R90T60C10	11.6	46.5	0.6	41.3	-
D-R50T30C10	9.0	13.0	-	6.5	71.5
D-R90T30C10	3.4	5.3	-	22.4	68.9
D-R90T60C10	3.0	3.9	-	20.4	72.7

Table 6. Quantities of the major phases shown in Table 5, normalized to ignited binder mass (in g/100g paste)

Sample	MgO	Brucite	Nesquehonite	Hydromagnesite	Calcite
M-R50T30C10	48.6	39.5	0.4	2.1	-
M-R90T30C10	31.4	38.8	6.8	25.9	-
M-R90T60C10	12.9	51.9	0.7	46.1	-
D-R50T30C10	7.7	11.1	-	5.5	61.0
D-R90T30C10	3.2	5.0	-	21.0	64.6
D-R90T60C10	2.7	3.5	-	18.5	66.0

Appendix: Calculation of the energy needed for the production of 1 ton of RMC and D800

1. The heat absorption with respect to the decomposition of magnesite and dolomite:

$$Q_{(\text{magnesite})} = \Delta H = \Delta H_{298}^{\ominus} = 100.6 \text{ kJ/mol}$$

$$Q_{(\text{dolomite})} = \Delta H = \Delta H_{298}^{\ominus} = 128.9 \text{ kJ/mol}$$

2. The amount of energy needed to heat CO_2 , MgO and CaCO_3 :

$$Q_{(\text{CO}_2)} = \int_{298}^{1073} c_p dT = 36.9 \text{ kJ/mol}$$

$$Q_{(\text{MgO})} = \int_{298}^{1073} c_p dT = 36.7 \text{ kJ/mol}$$

$$Q_{(\text{CaCO}_3)} = \int_{298}^{1073} c_p dT = 87.2 \text{ kJ/mol}$$

3. Theoretical power consumption during the calcination of magnesite and dolomite:

$$Q_{\text{Total (magnesite)}} = Q_{(\text{magnesite})} + Q_{(\text{CO}_2)} + Q_{(\text{MgO})} = 174.2 \text{ kJ/mol}$$

$$\text{To produce 1 ton of MgO (RMC): } 174.2 \text{ kJ/mol} / M_{(\text{MgO})} = 4355 \text{ kJ/kg} = 1209 \text{ kWh/t}$$

$$Q_{\text{Total (dolomite)}} = Q_{(\text{dolomite})} + Q_{(\text{CO}_2)} + Q_{(\text{MgO})} + Q_{(\text{CaCO}_3)} = 289.7 \text{ kJ/mol}$$

$$\text{To produce 1 ton of calcined dolomite (D800): } 289.7 \text{ kJ/mol} / M(\text{D800}) = 2069 \text{ kJ/kg} = 574 \text{ kWh/t}$$

4. The amount of coal needed for the production of 1 ton of RMC and D800 (i.e. containing MgO and CaCO_3) according to fuel comparison values reported by the European Nuclear Society (ENS):

$$\text{Coal}_{(\text{RMC})} = 1209 \text{ kWh/t} \times 0.125 \text{ kg/kWh} = 151.1 \text{ kg/tonne}$$

$$\text{Coal}_{(\text{D800})} = 574 \text{ kWh/t} \times 0.125 \text{ kg/kWh} = 71.8 \text{ kg/tonne}$$