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Dung, Nguyen Tien; Unluer, Cise

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Improving the carbonation of reactive MgO cement concrete via the use of NaHCO₃ and NaCl

N.T. Dung, Ph.D.¹ and C. Unluer, Ph.D.²

¹ Research Fellow, School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798, Email: tiendungnguyen@ntu.edu.sg

² Lecturer, School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798 (corresponding author), Email: ucise@ntu.edu.sg

Abstract

The performance of reactive MgO cement (RMC)-based concrete formulations is determined by the carbonation process, which is hindered by the inadequate CO₂ dissolution in the pore solution. This study addressed the improvement of carbonation and associated performance of carbonated RMC-based concrete samples via the introduction of sodium bicarbonate (SBC) and sodium chloride (SC). The use of these additives increased the initial pH, which accelerated the dissolution of CO₂ within the pore solution. The influence of SBC and SC on the progress of hydration was evaluated by isothermal calorimetry and pH measurements. Mechanical performance results were supported by x-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM), which identified the formation and morphology of final phases. The presence of SBC and SC enhanced the dissolution of CO₂ and improved the content and morphology of carbonate phases, leading to the formation of a strong carbonate network that increased sample performance by >100% at 28 days.

26 **Keywords:** MgO; Carbonation; Compressive strength; Dissolution; pH; Morphology

Introduction

The rapidly rising consumption of Portland cement (PC) in line with the increasing infrastructure demand on a global level has contributed to the undesirable emissions of anthropogenic carbon dioxide (CO_2) into the atmosphere. The development of alternative binders that can enable permanent CO_2 sequestration is one of the most promising methods to reduce atmospheric CO_2 . Reactive magnesium oxide (MgO) cement (RMC), mainly produced through the calcination of Mg-bearing minerals or synthesized from seawater or reject brine (Birchal et al. 2000; Ruan and Unluer 2016), can hydrate and react with CO_2 to form stable carbonate phases during the hardening process. The hydration of RMC forms $\text{Mg}(\text{OH})_{2(\text{aq},\text{s})}$, accompanied with an increase in the pH of the pore solution, which stimulates the diffusion and solubility of CO_2 in the pore space. The reaction between Mg^{2+} and CO_3^{2-} forms a range of hydrated magnesium carbonates (HMCs). Nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), hydromagnesite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), dypingite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$), and artinite ($\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$) are some of the most common HMCs, which lead to strength gain in carbonated RMC formulations through the pore filling effect of their expansive formation that reduces the overall pore volume and the binding capacity of HMC crystals that form an interconnected network. Hydration and carbonation reactions are critical for the strength development of RMC formulations as they control the degree of HMC formation.

Most of the studies focusing on the carbonation of RMC systems have indicated the rapid strength development of the prepared formulations under accelerated carbonation curing conditions that involved CO_2 concentrations ranging between 5 and 20% (Dung and Unluer 2016; Dung and Unluer 2017a; Dung and Unluer 2017b; Dung and Unluer 2017c; Liska and

Al-Tabbaa 2012; Liska et al. 2012a; Liska et al. 2012b; Liska et al. 2008; Ruan and Unluer 2017; Unluer and Al-Tabbaa 2013; Unluer and Al-Tabbaa 2014). RMC samples subjected to accelerated carbonation curing showed significantly higher strengths than those cured under ambient conditions. As the length of curing and the associated degree of carbonation increased, the carbonated samples gained strengths up to 7 times higher than samples cured under ambient conditions, showing that strength development was mainly due to carbonation rather than hydration (Dung and Unluer 2016; Dung and Unluer 2017a). Although the use of hydration agents (Dung and Unluer 2017a), high temperature pre-curing (Dung and Unluer 2017d) and accelerated carbonation conditions (Dung and Unluer 2016) have improved the mechanical performance of RMC-based concrete, phase quantification performed after the curing process still revealed large amounts of residual uncarbonated $\text{Mg}(\text{OH})_{2(s)}$ (brucite) within the samples. Previous research (Dung and Unluer 2016; Dung and Unluer 2017a) reported that up to 55% of the final binder phase was composed of uncarbonated brucite after 14 days of curing. These high contents of unreacted brucite highlight the inefficient use of RMC as a binder, which limits the strength development of concrete formulations.

Understanding the carbonation mechanism and identifying its limitations is critical for increasing the utility of RMC as a binder. In low pH conditions, the overall conversion of magnesium ions into carbonates is limited by the extent of the dissociation of carbonic acid into bicarbonate or carbonate ions (Park 2005). Therefore, the overall conversion of magnesium ions into carbonates is limited as the precipitation of brucite and formation of HMCs reduce the pH of the pore solution, thereby lowering the dissolution of CO_2 . This presents a constraint in the progress of carbonation within RMC formulations, hindering their continuous strength development.

This study proposes a method to increase the dissolution of CO_2 within the pore system and promote the reaction of Mg^{2+} and CO_3^{2-} to improve the carbonation and associated strength gain of RMC-based formulations. The carbonation reaction can be enhanced by increasing the pH via the use of sodium bicarbonate (NaHCO_3) and sodium chloride (NaCl), which have been previously reported to improve the carbonation of other Mg-based systems involving olivine and serpentine (Gadikota et al. 2014; Matter and Kelemen 2009; Park 2005). The incorporation of NaHCO_3 in RMC systems provides HCO_3^- ions, enabling the continuation of the carbonation reaction and shifting the equilibrium towards the production of additional carbonate ions available to react with the dissolved Mg^{2+} ions. The initially introduced HCO_3^- can also have a catalyzing effect on the dissolution of brucite at early stages due to the formation of multidentate mononuclear surface complexes that destabilize Mg-O bonds and the water coordination of Mg atoms at the surface (Pokrovsky et al. 2005). The reaction of the dissolved Mg^{2+} with HCO_3^- provided via the addition of NaHCO_3 leads to the formation of HMCs, thereby increasing the pH through the release of hydroxide ions. On the other hand, the use of NaCl not only provides a high initial pH, but also enhances the dissolution of MgO by weakening the bond within MgO under the presence of Cl^- , which disrupts the crystal structure of the mineral and facilitates its dissolution (O'Connor et al. 2004).

Utilizing the mechanism presented above, the performance and microstructural development of carbonated RMC concrete formulations involving the use of NaHCO_3 and NaCl were studied. Concrete samples with and without NaHCO_3 and NaCl were prepared and subjected to carbonation curing under a CO_2 concentration of 10% for up to 28 days. The influence of these additives on the hydration kinetics of MgO was evaluated by isothermal calorimetry and pH measurements. In addition to compressive strength testing, the hydration/carbonation products and the microstructural development of samples were investigated via x-ray

diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

Materials and Methodology

Materials

RMC, provided by Richard Baker Harrison (UK), was produced at around 1000 °C. Table 1 presents the chemical and physical properties of RMC, whose reactivity (i.e. measured by the time required for the neutralization of 0.25 M of acetic acid by 5 grams of RMC (Shand 2006)) was recorded as 520 seconds. Sodium bicarbonate (SBC) and sodium chloride (SC), obtained from VWR (Singapore), were used at a concentration of 0.05 M to promote the carbonation process. Course aggregates used in this study were saturated surface dry gravel with a particle size of 4.7–9.5 mm. Fine aggregates were not included in the mix compositions to enable the extraction of carbonated paste from the concrete samples without any contamination and to accurately quantify the hydrate and carbonate phases.

Methodology

Table 2 lists the compositions of the concrete samples prepared under this study. The ratio of solution to binder was fixed at 0.7 for all samples. The control sample (H₂O) was prepared to provide a comparison with samples SBC (using 0.05 M SBC solution), SC (using 0.05 M SC solution) and SBC.SC (using 0.05 M SBC and 0.05 M SC solution). The initial pH of H₂O,

SBC, SC and SBC.SC solutions were recorded as 7.80, 8.84, 8.57 and 8.67, respectively. Before casting the concrete samples, corresponding pastes were prepared to study the effects of SBC and SC on the hydration of MgO via isothermal calorimetry and pH measurements. For the preparation of concrete samples, SBC and SC were first dissolved in the mixing solution before being mixed with the dry materials. After they were cast into 50×50×50 mm cubic molds, consolidated by a vibrating table, and finished by trowel, the prepared concrete samples were cured in an incubator set at 10% CO₂, 80±5% relative humidity and 30±2 °C. All samples were demoulded after 24 hours and continuously subjected to the same conditions for up to 28 days.

Isothermal calorimetry

Isothermal calorimetry was measured at 30 °C by an I-Cal 2000 High Precision Calorimeter as per ASTM C1702 – 15a (2015). The paste samples were prepared by mixing RMC with water or SBC/SC solutions, which were previously heated to 30 °C in order to produce mixes at the same temperature as the measurement temperature, and were immediately placed into the calorimeter to record the heat flow and cumulative heat of hydration.

pH measurement

Paste samples were prepared and exposed to carbonation curing (10% CO₂, 80±5% relative humidity and 30±2 °C) for up to 28 days for the measurement of pH. The pH values of samples were determined at different ages by crushing and grinding the samples and

dispersing the fragments in water. After 20 minutes of mixing, the solids were filtered through a vacuum and the pH was measured by using a Mettler Toledo pH meter with an accuracy of ± 0.01 . All the measurements were conducted in triplicates and the average values were recorded, resulting in a deviation of < 0.03 .

Compressive strength

Three samples were tested for the compressive strength of each formulation, which were cured for 3, 7, 14 and 28 days. The test was conducted by Toni Technik Baustoffprüfsysteme machine at a constant loading rate of 55 kN/min.

XRD, TGA and SEM analyses

Fragments were obtained from the samples that were tested for their compressive strength. These sections were immersed in acetone for 24 hours to stop hydration and dried under vacuum for 24 hours to prepare for microstructural analysis. The samples were then ground to pass through a 75 μm sieve for XRD and TGA.

The ground powders were characterized by XRD via a Philips PW 1800 spectrometer under Cu K α radiation (40 kV, 30 mA) and a scanning rate of 0.04° 2 θ /step to identify crystalline phases in the range of 5-80° 2 θ . The RIR technique (Hubbard and Snyder 1988; Johnson and Zhou 2000; Snyder 1992) was applied for the quantitative analysis of selected phases, as

explained further in (Liska and Al-Tabbaa 2009). The RIR results for each sample were reported by calculating the average of 2 measurements with a standard deviation of < 3%.

TGA was performed by using a Perkin Elmer TGA 4000 equipment, operated within a temperature range of 50 to 950 °C, with a heating rate of 10 °C/min under nitrogen flow. In preparation for SEM analysis, the vacuum dried samples were placed onto aluminum stubs, after which a thin gold coating was applied. The morphologies of the hydration and carbonation products within each sample were observed via SEM images obtained via a Zeiss Evo 50 microscope.

Results

Hydration kinetics

Fig. 1 (a) and (b) show the heat flow and the cumulative heat of all pastes during the first 24 hours of hydration, respectively. As seen in Fig. 1 (a), the dissolution of MgO took place a few minutes after mixing for all samples. The higher initial pH of samples including SBC and/or SC resulted in a lower heat release than the control sample. The presence of the Cl⁻ ion in the SC and SBC.SC samples weakened the Mg-O bond to facilitate the dissolution of MgO and thereby led to a similar initial dissolution rate as the control sample during the first few hours. While the presence of the Cl⁻ ion enabled the SC and SBC.SC samples to reach a similar hydration degree with the control sample in the first 2 hours, the cumulative heat curves in Fig. 1 (b) revealed the slightly higher heat released by the control and SC samples, in comparison to SBC and SBC.SC, after 24 hours of hydration. This difference in the

hydration degrees could be associated with the role of SBC, which reduced the overall hydration by increasing the initial pH, whose details are discussed further in the next section.

pH

The pH values of all samples measured at different durations, which represent the average of three measurements with a deviation less than 0.03, are listed in Table 3. The presence of Na⁺ ions resulted in higher pH values in SBC, SC and SBC.SC solutions than in water (8.57-8.84 vs. 7.80). Accordingly, the initial pH of the SBC, SC and SBC.SC samples was higher than that of the control sample (10.48-10.61 vs. 10.22), enabled by the presence of the additives. This raise in the pH of the fresh pastes was attributed to the increased dissolution of MgO and generation of OH⁻. The highest pH values demonstrated by the SBC and SBC.SC samples could be associated with the reaction between the dissolved Mg²⁺ and HCO₃⁻ from SBC, which led to the formation of HMCs and release of hydroxide ions. When compared to the pH values of the fresh pastes, a decrease in pH was observed in the first 3 days of carbonation in all samples, during which the dissolution of CO₂ in the pore solution neutralized the alkaline solutions and reduced the pH (Ayoub et al. 1999). Throughout the carbonation process, the reaction between the dissolved Mg²⁺ and CO₃²⁻ released Na⁺ and OH⁻, thereby raising the pH of the pore solution, which was neutralized and maintained within a narrow range by the dissolution of CO₂.

The use of SBC and/or SC stimulated the dissolution of CO₂ even at early ages, as revealed by the higher reduction in their initial pH values (i.e. fresh paste vs. 1-day pH), in comparison to the control sample. Despite its lower initial pH, the control sample demonstrated a similar

pH as the SBC, SC and SBC.SC samples as the duration of carbonation increased. A comparison of the initial pH values of the fresh pastes with the pH at 28 days revealed a noticeable reduction in the pH of samples containing SBC and/or SC, whereas the pH of the control sample remained relatively stable. This difference in the reduction of pH could be an indication of the carbonation potential of each sample, highlighting the higher contents of CO₂ dissolved in samples containing SBC and/or SC.

Compressive strength

The compressive strength development of all concrete samples subjected to 28 days of carbonation curing is shown in Fig. 2. The strength of all samples increased with time, which was attributed to the continuous carbonation and formation of HMCs over 28 days. Although all samples generally demonstrated similar rates of strength gain during the first 14 days of curing, samples containing SBC and/or SC outperformed the control sample in the longer durations. In line with the findings of previous studies (Dung and Unluer 2016; Dung and Unluer 2017a; Dung and Unluer 2017d), the strength development of the control sample slowed down with time, which was associated with the reduction in the rate of carbonation. A different scenario was observed in samples containing SBC and/or SC, which indicated a continuous progress carbonation at longer durations (> 14 days), leading to significantly higher strengths than the control sample.

A comparison of the early strengths of all samples at 3 days revealed the strength of the control sample as 11 MPa, while those of the SBC, SC and SBC.SC samples ranged between 6-9 MPa. These lower early strengths of samples containing SBC and/or SC were associated

with their initially high pH values, which lowered the dissolution of MgO and resulted in lower brucite contents available for carbonation. The trend in strength development changed as the curing duration increased, revealing higher strengths for samples containing SBC and/or SC when compared to the control sample at 7 days (12-17 vs. 11 MPa) onwards. The difference in the strength values was more obvious at longer durations, revealing around 25-110% higher strengths than the control sample at 28 days (30-50 vs. 24 MPa). The simultaneous use of SBC and SC in the SBC.SC sample led to the highest strengths amongst all samples, which was related with the highest initial pH of this sample. The increase in the initial pH improved the dissolution of CO₂ (Ambreen Aslam 2016; Leitao et al. 2006), which resulted in the enhancement of the carbonation process and associated strength gain within the SBC, SC and SBC.SC samples. The combination of SBC and SC in the SBC.SC sample led to a higher pH and increased availability of HCO₃⁻ via the use of SBC, which translated into the higher conversion degrees of initial Mg-phases into strength providing carbonates.

XRD

Fig. 3 illustrates the XRD patterns of carbonated samples at 28 days. Nesquehonite, dypingite and hydromagnesite were seen in all samples due to the use of carbonation curing. In addition to HMCs, unhydrated MgO and uncarbonated Mg(OH)₂ was observed in all samples, whose main peaks were located at 42.9° and 38.1° 2θ, respectively. Based on the intensity of the internal standard (fluorite, main peak at 28.3° 2θ), a lower amount of uncarbonated brucite was observed in the SBC, SC and SBC.SC samples when compared to the control sample. However, an opposite trend was observed in the amount of residual MgO, which was lowest

in the control sample. The unhydrated MgO and uncarbonated Mg(OH)₂ contents of all samples after 28 days of carbonation was quantified and reported in Table 4.

When compared to the control sample (H₂O), the use of SBC and/or SC led to slightly higher unhydrated MgO contents (35.7-37.4 vs. 34%). The lower hydration of samples including SBC and/or SC was associated with the higher initial pH of these samples, as revealed earlier in Table 3. Alternatively, the addition of SBC and SC significantly enhanced the carbonation reaction, which was evident from the reduced uncarbonated brucite contents within the SBC, SC and SBC.SC samples. In line with the compressive strength results, SBC was more influential in promoting carbonation than SC, whose addition had a less obvious effect on the amount of residual brucite. The enhancement provided via the use of SBC was due to the increased initial pH, which was beneficial for CO₂ dissolution (Ambreen Aslam 2016; Leitao et al. 2006). This was further supported with the provision of HCO₃⁻ ions within the initial mix, thereby enabling the continuation of the carbonation reaction and shifting the equilibrium towards the production of additional carbonate ions that reacted with the dissolved Mg²⁺ ions to form HMCs. The simultaneous use of SBC and SC in the SBC.SC sample, which had also demonstrated the best mechanical performance amongst all samples, significantly accelerated the carbonation reaction, as shown by the 25% reduction in the amount of uncarbonated brucite from 50.2% in the control sample to 37.8%. This improvement in the carbonation process was attributed to the higher initial pH enabled via the introduction of SBC and SC, which promoted the dissolution of CO₂ in the pore solution and the subsequent carbonation reaction.

299 TGA

300

301 The mass loss and heat flow curves of samples after 28 days of carbonation are illustrated in
302 Fig. 4. Since all the samples were thoroughly dried before analysis, the higher mass loss of
303 samples containing SBC and/or SC in comparison to the control sample was an indication of
304 their higher reaction degrees. The thermal decomposition of hydrate and carbonate phases
305 was analyzed based on the endothermic peaks. In addition to an endothermic peak at 120 °C,
306 another one corresponding to the dehydration of HMCs was observed at 220 °C in the SBC
307 and SBC.SC samples. A distinct endothermic peak at around ~380-400 °C was responsible
308 for the dehydroxylation of uncarbonated brucite along with the dehydroxylation (e.g.
309 hydromagnesite/dypingite) and decarbonation (e.g. nesquehonite) of HMCs. A broader peak
310 observed at ~750 °C corresponded to the decarbonation of HMCs. The dehydration,
311 dehydroxylation and decarbonation steps observed in all samples, as summarized below,
312 were in agreement with the findings of earlier studies (Ballirano et al. 2010; Frost et al. 2008;
313 Frost and Palmer 2011; Hollingbery and Hull 2010; Jauffret et al. 2015; Purwajanti et al.
314 2015; Vágvölgyi et al. 2008).

315

316 (i) 50 to 300 °C: Dehydration of water bonded to HMCs ($x\text{MgCO}_3 \cdot y\text{Mg}(\text{OH})_2 \cdot z\text{H}_2\text{O}$), as
317 shown in Equation 1 (Ballirano et al. 2010; Frost et al. 2008; Frost and Palmer 2011; Jauffret
318 et al. 2015; Purwajanti et al. 2015; Vágvölgyi et al. 2008).

319

321

322 (ii) 300 to 500 °C: Dehydroxylation of uncarbonated brucite, as shown in Equation 2;
323 dehydroxylation of HMCs (e.g. $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$) and

MgCO₃·Mg(OH)₂·3H₂O), as shown in Equation 3; and decarbonation of HMCs (MgCO₃·3H₂O), as shown in Equation 4 (Ballirano et al. 2010; Frost et al. 2008; Frost and Palmer 2011; Hollingbery and Hull 2010; Jauffret et al. 2015).

(iii) 500 to 900 °C: Decarbonation of magnesium carbonate, as shown in Equation 4 (Frost et al. 2008; Jauffret et al. 2015).

The total mass loss and the mass loss associated with each decomposition reaction are shown in Table 5. The dehydroxylation and decarbonation steps occurring within 300-500 °C led to the highest mass loss in all samples. The mass loss due to the decomposition of carbonate phases was calculated by subtracting the mass loss associated with the decomposition of brucite (i.e. calculated from the brucite content presented in Table 4) from the total mass loss. When the brucite contents listed in Table 4 as well as the calorimetry results in Figure 1 were observed, it could be seen that the addition of SBC and/or SC did not make a significant contribution to the hydration process. As the brucite contents within SBC, SC and SBC.SC samples were not higher than the control sample at 28 days (Table 4), the increase in the mass loss within the 300-500 °C range could be mainly associated with the loss of CO₂ within samples containing SBC and/or SC.

As seen from the results displayed in Table 5, the inclusion of SBC and/or SC in the prepared RMC formulations led to an increase in the mass loss. When compared with the control sample, the mass loss due to the decomposition of HMCs was up to 56% higher (17.5 vs. 25.2-27.4%) in samples containing SBC and/or SC. Most evident in the SBC.SC sample, these higher mass loss values associated with the decomposition of carbonate phases were a clear indication of the enhancement of the reaction mechanisms and corresponding mechanical performance demonstrated by samples involving the use of SBC and/or SC.

Another parameter derived from the TGA data was the efficiency of HMC formation (E_C), an indication of the amount of HMC as a percentage of the initial RMC, which was used to evaluate the effect of the introduced additives (i.e. SBC and SC) on the carbonation of RMC samples. The calculation of E_C was performed according to Equation 5, where P_{HMCs} represents the percentage of mass loss corresponding to the decomposition of HMCs and P_{RMC} represents the percentage of the final mass at 900 °C (i.e. residual MgO). As seen in Table 5, the introduction of SBC increased the HMC formation efficiency of the control sample by 54%, from a E_C value of 0.26 to 0.4. This figure increased by up to 73% to reach 0.45 with the simultaneous introduction of SBC and SC in the SBC.SC sample.

$$E_C = P_{HMCs}/P_{RMC} \quad (5)$$

Microstructural analysis

Fig. 5 shows microstructural images that demonstrate the phase formations within carbonated samples at 28 days. The formation of needle-like nesquehonite dominated in all samples,

accompanied with disk/rose-like hydromagnesite/dypingite. The pore filling effect of these carbonates, coupled with the formation of a dense interlocked network was the main source of strength development within RMC formulations. Disk-like hydromagnesite/dypingite with a diameter of $\sim 1\text{-}2\text{ }\mu\text{m}$ blended amongst nesquehonite needles with a diameter of $\sim 0.5\text{-}1\text{ }\mu\text{m}$ was observed in the control sample (Fig. 5 (a)). Differing from the control sample, the SBC, SC and SBC.SC samples presented a denser layer of carbonates with larger crystal sizes. In both the SBC (Fig. 5 (b)) and SC (Fig. 5 (c)) samples, disk-like hydromagnesite/dypingite with a diameter of $\sim 3\text{ }\mu\text{m}$ was seen to form on top of a solid layer of nesquehonite. The intermingling of individual nesquehonite needles, with a diameter of $\sim 1\text{ }\mu\text{m}$ and a length of up to $7\text{-}8\text{ }\mu\text{m}$, into a dense wall-like plate within the SBC.SC sample (Fig. 5 (d)) has contributed to the highest strength results achieved by this sample.

Conclusions

The performance of carbonated RMC-based concrete depends on the extent of the hydration and carbonation processes, as well as the morphology of final carbonate phases. Moving on from previous attempts that focused on the improvement of the hydration reaction to provide an increased amount of brucite available for carbonation (Dung and Unluer 2016; Dung and Unluer 2017a), this study aimed to improve the carbonation process and associated mechanical performance of RMC samples. The main issue to overcome was the low pH of RMC formulations, which can limit the dissolution of CO_2 into the pore solution, thereby hindering the continuation of carbonation. Increased carbonation was to be achieved via the introduction of two additives, sodium bicarbonate (SBC) and sodium chloride (SC), into the initial mix design.

399

400 The use of these additives was designed to increase the initial pH and accelerate the
401 dissolution of CO₂ within the pore solution, which translated into a higher degree of
402 carbonation and improved strength development. Furthermore, the incorporation of SBC in
403 RMC systems provided additional HCO₃⁻ ions, enabling the continuation of the carbonation
404 reaction and promoting the production of carbonate ions to react with the dissolved Mg²⁺
405 ions. While the use of SBC and SC slightly lowered the hydration degree of RMC samples at
406 early ages due to their initially higher pH, this was not an issue under carbonation conditions,
407 as revealed by the similar uncarbonated MgO contents of all samples. The introduction of
408 SBC and SC not only proved to increase the carbonate content of the designed RMC
409 formulations, but also improved the morphology of the final phases by revealing dense
410 microstructures composed of large interconnected crystals. In addition to their extensive
411 formation under the presence of SBC and SC, the firm bonds established amongst the
412 carbonate phases contributed to the overall strength development.

413

414 Further studies on the development of RMC samples containing these additives shall focus on
415 the long-term durability of the proposed formulations under various conditions. These
416 durability studies will not only highlight the performance of RMC as a binder, but also shed
417 light on the stability of HMC phases within different compositions.

418

419

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421

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List of Tables

Table 1. Chemical composition and physical properties of RMC.

	Chemical composition (%)							Physical properties	
	MgO	SiO ₂	CaO	R ₂ O ₃	K ₂ O	Na ₂ O	LOI	Specific gravity (g/cm ³)	Specific surface area (m ² /g)
RMC	>91.5	2.0	1.6	1.0	-	-	4.0	3.0	16.3

Table 2. Compositions of concrete samples investigated in this study.

Mix label	Mix proportion (kg)					
	H ₂ O	SBC	SC	SBC (0.05 M)	RMC	Coarse
		(0.05 M)	(0.05 M)	& SC (0.05 M)		aggregates
H ₂ O	315	-	-	-		
SBC	-	315	-	-	450	1360
SC	-	-	315	-		
SBC.SC	-	-	-	315		

Table 3. pH values of all samples during 28 days of carbonation.

Mix label	pH value						
	Initial solution	Fresh paste	1-day	3-day	7-day	14-day	28-day
H ₂ O	7.80	10.22	10.18	10.10	10.13	10.16	10.23
SBC	8.84	10.54	10.22	10.13	10.16	10.21	10.33
SC	8.57	10.48	10.25	10.20	10.26	10.20	10.24
SBC.SC	8.67	10.61	10.24	10.23	10.34	10.20	10.28

Table 4. MgO and Mg(OH)₂ contents of all samples obtained by XRD after 28 days of carbonation.

Mix label	MgO (%)	Brucite (%)
H ₂ O	33.95	50.19
SBC	36.34	39.70
SC	37.42	47.04
SBC.SC	35.72	37.83

Table 5. Mass loss and carbonation degrees of all samples obtained by TGA after 28 days of carbonation.

Mix label	Mass loss (wt.%)						E _C
	50-300 °C	300-500 °C	500-900 °C	Brucite	HMCs	Total	
H ₂ O	4.63	25.30	3.19	15.58	17.54	33.12	0.26
SBC	8.43	26.22	2.88	12.32	25.21	37.53	0.40
SC	11.17	27.41	3.01	14.60	26.99	41.59	0.46
SBC.SC	8.97	27.32	2.83	11.74	27.38	39.12	0.45