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Ruan, Shaoqin

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**DEVELOPMENT OF REACTIVE MAGNESIA
CEMENT-BASED FORMULATIONS WITH
IMPROVED PERFORMANCE &
SUSTAINABILITY**

**RUAN SHAOQIN
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING**

2019

DEVELOPMENT OF REACTIVE MAGNESIA CEMENT-BASED FORMULATIONS WITH IMPROVED PERFORMANCE & SUSTAINABILITY

RUAN SHAOQIN

School of Civil and Environmental Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirements for the degree of
Doctor of Philosophy

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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RUAN SHAOQIN

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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.....

Date

ASoh, / CUnluer

.....

Goh Teck Chee, Anthony / Cise Unluer

Authorship Attribution Statement

This thesis contains material from 6 papers published in the following peer-reviewed journals where I was the first and/or corresponding author.

Chapter 4 is published as **(1)** S. Ruan, C. Unluer, Effect of air entrainment on the performance of reactive MgO and PC mixes, *Construction and Building Materials* 142 (2017) 221-232. DOI: 10.1016/j.conbuildmat.2017.03.068. **(2)** S. Ruan, C. Unluer, Influence of mix design on the carbonation, mechanical properties and microstructure of reactive MgO cement-based concrete, *Cement and Concrete Composites* 80 (2017) 104-114. DOI: 10.1016/j.cemconcomp.2017.03.004. **(3)** S. Ruan, C. Unluer, Influence of supplementary cementitious materials on the performance and environmental impacts of reactive magnesia cement concrete, *Journal of Cleaner Production* 159 (2017) 62-73. DOI: 10.1016/j.jclepro.2017.05.044.

The contributions of the co-authors are as follows:

- Dr Cise Unluer provided the initial project direction
- All the sample preparations and mechanical tests were conducted by me in the Protective Engineering Lab at the School of Civil and Environmental Engineering.
- The thermal conductivity test was conducted by me in the Civil Engineering Materials Lab at the School of Civil and Environmental Engineering.
- All the microstructural analysis including scanning electron microscope was conducted by me in the Environmental Lab at the School of Civil and Environmental Engineering.
- Dr Cise Unluer provided guidance in the interpretation of the results.
- I wrote the drafts of the manuscript. The manuscript was revised by Dr Cise Unluer.

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- Prof Yang En-Hua and Dr Cise Unluer provided the initial project direction.
- Mr Liu Jiawei prepared the samples for testing.
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- The rheology test was conducted by Dr Qiu Jishen.
- The mechanical test was conducted by Dr Qiu Jishen and me in the Protective Engineering Lab at the School of Civil and Environmental Engineering.
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- Mr Yang Yang cultivated the bacteria and provided it in the self-healing procedure.

- Dr Qiu Jishen and Prof Yang En-hua provided guidance in the interpretation of the self-healing and strain-hardening results.
- I wrote the drafts of the manuscript. The manuscript was revised by Prof Yang En-hua, Prof Chu Jian and Dr Cise Unluer.

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- Dr Cise Unluer provided the initial project direction
- The collection of life cycle inventories was conducted by me
- The calculations and analysis of environmental impacts were performed in the computer lab at the School of Civil and Environmental Engineering.
- Dr Cise Unluer provided guidance in the interpretation of the results.
- Dr Cise Unluer revised and edited the manuscripts.

20/3/2019

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Date

.....
RUAN SHAOQIN

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ABSTRACT

Portland cement (PC) production is accountable for 5-7% of anthropogenic carbon dioxide (CO₂) emissions. This has led to a growing interest in sustainable practices in line with the increased pressure on the cement and construction industries to develop alternative technologies with reduced CO₂ emissions. An example of new binders developed with this goal in mind is reactive magnesia (MgO), which is produced at lower temperatures than PC (700-1000 vs. 1450 °C), and has the ability to absorb CO₂ in the form of stable carbonates during accelerated CO₂ curing and gain strength accordingly. The presented research incorporates two main areas involving the use of reactive magnesia within the construction industry: (i) Enhancement of carbon sequestration, mechanical performance, strain-hardening and self-healing behaviors of reactive magnesia-based and PC formulations under 10% CO₂, water, air and bacterial curing, and (ii) Life cycle analysis of reactive magnesia production in comparison to PC.

The first area focused on the enhancement of the carbonation process, mechanical performance, microstructural development, and strain hardening and self-healing potentials of reactive magnesia-based formulations under 10% CO₂, water, air and bacterial curing, with PC formulations included as a comparison in this area. This investigation involved the evaluation of the influence of various parameters including mix design (i.e. cement, water and aggregate contents), introduction of additives (i.e. air-entrained agent (AEA), PFA and GGBS), use of alternative sources for reactive magnesia (i.e. calcined dolomite), and incorporation of fibers under 10% CO₂, water, air and bacterial curing on the performance of reactive magnesia-based and PC mixes. The outcomes of this research were presented in terms of fresh and hardened properties involving the measurement of porosity, density, workability, thermal conductivity, water sorptivity, rheology, resonance frequency, crack healing efficiency, hydration and carbonation reaction mechanisms, mechanical properties and microstructural characterization of various reactive magnesia-based concrete mixes.

Overall, the results indicated that introduction of AEA reduced early strength of reactive magnesia formulations due to increased air contents under 10% CO₂ curing. This was compensated by increased CO₂ penetration, carbonation and strength gain in longer periods. Samples in which 50% of the binder component was replaced by PFA subjected to 10% CO₂ curing

indicated the highest strength development, which was associated with a reduction in sample porosity due to the filler effect of PFA as well as the formation of strength providing phases through the hydration and carbonation reactions. The use of calcined dolomite was also investigated as a new source of reactive magnesia within concrete mixes. The presence of undecomposed carbonate phases in dolomite facilitated the continuation of the hydration and carbonation reactions and both reactive magnesia and calcined dolomite samples benefited from the use of high humidity (90%), whereas elevated temperatures (60 °C) presented an advantage only in reactive magnesia samples under 10% CO₂ curing. The final section of this study led to the development of reactive magnesia based strain-hardening composites (SHC) via the use of 10% CO₂ curing, whose self-healing capacity was also demonstrated. The adequate binder content and w/b ratio necessary for desirable fiber dispersion was determined. The autogenous self-healing capacity of the developed binders under the presence of water and elevated CO₂ concentrations was highlighted, during which the formation of hydrated magnesium carbonates (HMCs) that were capable of sealing the cracks was observed. A subsequent investigation involved the use of microbial induced carbonate precipitation (MICP), which was more effective than the use of water and CO₂ in terms of crack healing efficiency in reactive magnesia-based samples, resulting in a high extent of healing products in a short time period.

The second area focused on the assessment of the environmental impacts of reactive magnesia and PC production. In terms of production, reactive magnesia had a lower impact on the overall ecosystem quality and resources than PC, but posed a larger damage to human health due to the high coal usage by most plants.

The research presented in this study contributed to the literature via the information generated on the relationship between the fresh and hardened properties of reactive magnesia formulations. This involved the identification of the influence of phase formations on the mechanical and microstructural development of reactive magnesia samples under 10% CO₂ curing. This study is novel as it is the first in the literature to investigate the environmental impacts of the production of reactive magnesia as a binder in comparison with PC, introduce several additives (AEA, PFA and GGBS) and alternative sources for magnesium (calcined dolomite) into reactive magnesia mixes and develop reactive magnesia-based strain hardening composites via the use of

accelerated CO₂ curing with the ability to undergo self-healing. The reported findings have indicated the high potential of reactive magnesia-based formulations to be used in various building applications based on their ability to be produced from alternative sources and gain strength via the sequestration of CO₂.

LIST OF PUBLICATIONS

All the publications derived from the work presented in this thesis are listed below:

1. S. Ruan, C. Unluer, Comparative life cycle assessment of reactive MgO and Portland cement production, *Journal of Cleaner Production* 137 (2016) 258-273.
2. S. Ruan, C. Unluer, Influence of mix design on the carbonation, mechanical properties and microstructure of reactive MgO cement-based concrete, *Cement and Concrete Composites* 80 (2017) 104-114.
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5. S. Ruan, J. Liu, E.-H. Yang, C. Unluer, Performance and microstructure of calcined dolomite and reactive magnesia-based concrete samples, *Journal of Materials in Civil Engineering* 29(12) (2017) 04017236.
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7. S. Ruan, C. Unluer, Comparison of the environmental impacts of reactive magnesia and calcined dolomite and their performance under different curing conditions, *Journal of Materials in Civil Engineering* 30(11) (2018) 04018279.
8. V. Rheinheimer, C. Unluer, J. Liu, S. Ruan, J. Pan, P.J. Monteiro, XPS study on the stability and transformation of hydrate and carbonate phases within MgO systems, *Materials* 10(1) (2017) 75.
9. S. Ruan, J. Qiu, Y. Weng, Y. Yang, E.-H. Yang, J. Chu, C. Unluer, The use

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10. J. Qiu, S. Ruan, C. Unluer, E.-H. Yang, Autogenous healing of fiber-reinforced reactive magnesia-based tensile strain-hardening composites, *Cement and Concrete Research* 115 (2019) 401-413.

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Chapter 1 INTRODUCTION

1.1 Research background

The increased concentrations of greenhouse gases in the atmosphere due to human activities have given rise to climate change, which is regarded as a major environmental concern. Apart from developed countries, emerging nations like China are experiencing a sudden increase in their CO₂ emissions to meet the demands of their growing population. Increasing at an average annual rate of ~4.4% in the last 5 years (Statista 2016), Portland cement (PC) production is accountable for approximately 5-7% of anthropogenic CO₂ emissions (Benhelal, Zahedi et al. 2013, Turner and Collins 2013). The manufacture of every tonne of PC results in the emission of ~0.9 tonne of CO₂ (Van den Heede and De Belie 2012, Benhelal, Zahedi et al. 2013). This has led to a growing interest in sustainable practices in line with the increased pressure on industries to develop alternative technologies with reduced CO₂ emissions.

Around 60% of the CO₂ emitted by cement plants is derived from the calcination of limestone (i.e. decomposition of CaCO₃ into CaO and CO₂), whereas the rest is from the energy consumed during this process (Van Oss and Padovani 2002, Allwood, Cullen et al. 2010, Boesch and Hellweg 2010). The extent of CO₂ emitted is heavily dependent on the manufacturing method and the type of fuel utilized during production (Marceau, Nisbet et al. 2006, Taylor, Tam et al. 2006, Hendrik and van Oss 2010, Valderrama, Granados et al. 2012). In addition to the CO₂ discharge, nitrogen oxides (NO_x), sulphur oxides (SO_x), cement kiln dust (CKD), particulate matter (PM), carbon monoxide (CO) and heavy metals are emitted into the atmosphere during cement production (Boesch and Hellweg 2010, Lei, Zhang et al. 2011, Magrama 2012, Valderrama, Granados et al. 2012, Wang 2013). A major source of air contaminants, 40% of PM emissions are from industrial origins.

PC plants account for approximately 15–27% of PM, 3–4% of sulfur dioxide (SO_2) and 8–12% of NO_x emissions in China (CEYEC 2001, Lei, Zhang et al. 2011, Li and Li 2013). Similarly in Europe, the production of 1 tonne of Type I PC results in the average emissions of 2.4 kg of NO_x , 0.6 kg of SO_2 and 2.7 kg of dust (Josa, Aguado et al. 2007). These emissions are mainly due to the impurities present within the raw materials and the combustion of fuels used during cement production (Steinberg 1985, EPA 1994, Oss and Padovani 2003). Furthermore, crude limestone contains a high amount of impurities (i.e. Fe_2O_3 , SiO_2 , Al_2O_3 and MgO) (Steinberg 1985), leading to the release of heavy metals during the calcination process.

Development of alternative cementitious materials with lower energy consumption and CO_2 emissions presents a promising solution in mitigating the environmental impacts of PC production. Recently developed reactive MgO cement (RMC) has gained popularity as an alternative construction material due to its sustainability advantages when compared with PC. The various aspects of RMC, which was developed and patented more than a decade ago (AJW 2003, Harrison 2008), have received coverage in the New Scientist (Pearce 2002) and the Guardian (Dyer 2003). Fig. 1.1 provides a summary of the timeline related to the use of MgO in the construction industry as reported by various commercial and research institutions (De Silva, Bucea et al. 2009, Mo, Deng et al. 2010, Mo and Panesar 2012, Panesar and Mo 2013, Mo, Deng et al. 2014, Mo and Panesar 2014). MgO can be classified as “reactive”, “hard-burned”, “dead-burned” or “fused” depending on the calcination temperature used during its production. Light-burned (i.e. reactive or caustic) MgO is produced at 700-1000 °C and has a very high specific surface area (SSA) and reactivity. The properties and applications of light-burned MgO have been reported in several studies (Jensen, Aaes et al. 1986, Birchal 2001, Garcia, Chimenos et al. 2004, Rotting, Cama et al. 2006, Chau and Li 2008, Caraballo, Roetting et al. 2009, Fukumoto, Sasaki et al. 2011, Jin and Al-Tabbaa 2014, Unluer and Al-Tabbaa 2014), including its use in cementitious materials (Vandeperre and Al-Tabbaa 2007, Vandeperre, Liska

et al. 2007, Vandeperre, Liska et al. 2008, Liska and Al-Tabbaa 2009, Unluer and Al-Tabbaa 2011, Mo and Panesar 2012). Hard-burned MgO is produced at 1000-1400 °C and has a relatively low SSA and reactivity. It is typically used in applications that exploit the expansion properties of MgO (Gao, Lu et al. 2008, Mo, Deng et al. 2014). Dead-burned MgO (periclase) is produced at 1400-2000 °C, has a low SSA and is unreactive (Wagh 2004). It is mainly used in refractories (Ghanbari Ahari, Sharp et al. 2002, Silva, Aneziris et al. 2011). Fused MgO is produced above 2000 °C, therefore possessing a low hydration energy, high thermal shock resistance and a compact structure. It is used in monolithic refractories and electrical insulating (Canterford 1985, Li, Zhang et al. 2015).

Fig. 1.1 Timeline of the usage of MgO within the cement industry (Unluer 2018)

The composition of RMC-based binders may include PC, pozzolans or various waste materials, depending on the intended use, ranging from structural applications to masonry units. Several studies focusing on the hydration (Vandeperre, Liska et al. 2008, Jin, Abdollahzadeh et al. 2013), carbonation (Vandeperre and Al-Tabbaa 2007, Liska, Vandeperre et al. 2008, Mo and Panesar 2012, Unluer 2012, Mo and Panesar 2013, Panesar and Mo 2013, Unluer and Al-Tabbaa 2013, Unluer and Al-Tabbaa 2014), microstructure (Vandeperre, Liska et al. 2008, Cwirzen and Habermehl-Cwirzen 2012, Mo and Panesar 2012), mechanical properties (Vandeperre, Liska et al. 2008, Li 2013) and durability performance (Cwirzen and Habermehl-Cwirzen 2012, Liska and Al-Tabbaa 2012, Li 2013) of various MgO cement formulations have been reported. The main applications of MgO within the construction industry include: (i) magnesium oxychloride (MOC) cements (also known as Sorel cements), which are used in fiber reinforced fire resistant boards (Sorrel and Armstrong 1976, Urwongse and Sorrell 1980); (ii) magnesium oxysulfate (MOS) cements used in lightweight insulation panels (Beaudoin and Feldman 1977, Beaudoin and Ramachandran 1978); (iii) magnesium phosphate (MAP) cements used in fire protection and rapid repairs (Ribeiro and Morelli 2009, Mestres and Ginebra 2011, Viani and Gualtieri 2014); and (iv) magnesium expansive additives (MEA) used to compensate concrete shrinkage in dam construction (Zheng, Xuehua et al. 1991, Gao, Lu et al. 2008, Mo, Deng et al. 2010, Gao, Xu et al. 2013, Mo, Deng et al. 2014). Recent research on the use of RMC has identified its ability to gain strength by carbonation, which has led to the development of porous cement-based applications with the ability to permanently sequester CO₂ during curing (Vandeperre, Liska et al. 2008, Liska and Al-Tabbaa 2009, Yi, Liska et al. 2012).

Main advantages of RMC include its: (i) ability to sequester CO₂ and gain strength by the formation of hydrated magnesium carbonates (HMCs), (ii) high fire resistance, (iii) high durability performance in extreme and aggressive environments, (iv) lower sensitivity to impurities enabling the use

of industrial by-products and (v) potential to be fully recycled when RMC is used alone as a binder (Mo and Panesar 2012, Unluer 2012, Mo and Panesar 2013, Unluer and Al-Tabbaa 2014). Major issues include unfamiliarity and insufficient track record compared to the high validation and market confidence in PC, which can be overcome with a well-planned research agenda generating long-term results. The role of RMC as a partial or complete substitute of PC in concrete (Vlasopoulos 2011, Li 2013) and masonry blocks (Liska 2009, Unluer and Al-Tabbaa 2011, Unluer 2012, Unluer and Al-Tabbaa 2014) has been investigated to a certain extent. The production and characterization of different sources of MgO and its performance in various blends have been reported (Schneider, Romer et al. 2011, Hassan 2013, Jin 2013, Pacheco-Torgal, Jalali et al. 2013). The use of RMC in these applications was shown to enhance carbonation, mechanical properties and durability, however, RMC formulations can only be prepared in a controlled environment with a high CO₂ concentration as the CO₂ level in air is relatively low (i.e. 0.04%), which inhibits their hardening and strength gain. Therefore, RMC formulations cannot be used in the bulk of the construction industry where cement is required to set and harden on site without accelerated carbonation, and RMC can only be used as a partial replacement of PC formulations, whereas in samples containing 100% RMC, some possible applications could be precast slabs, pavement or masonry blocks, where the pre-treatment of RMC samples via the use of high CO₂ concentration is possible.

The research presented in this report incorporates two main research areas involving the use of RMC within the construction industry: (i) Life cycle analysis (LCA) of RMC production in comparison to PC and (ii) Enhancement of carbon sequestration, mechanical performance, strain-hardening and self-healing behaviors of RMC-based formulations under different conditions. A summary of the structure of this study is illustrated in Fig. 1.2.

Fig. 1.2 Structure of the research project presented in this report

The first research task focused on the enhancement of the carbonation process, mechanical performance, microstructural development, and strain hardening and self-healing potentials of RMC-based formulations. This investigation involved the evaluation of the influence of various parameters including mix design (i.e. cement, water and aggregate contents), introduction of additives (i.e. air-entrained agent (AEA), PFA and GGBS), use of alternative sources for RMC (i.e. calcined dolomite), and incorporation of fibers under various curing conditions on the performance of RMC-based mixes. The outcomes of this research were presented in terms of fresh and hardened properties involving the measurement of porosity, density, workability, thermal conductivity, water sorptivity, rheology, resonance frequency, crack healing efficiency, hydration and carbonation reaction mechanisms, mechanical properties and microstructural characterization of various RMC-based concrete mixes. The second area focused on the assessment of the environmental impacts of RMC production by means of an LCA from a “cradle-to-gate” perspective. The outcomes of this research led to the identification of several key environmental indicators through different methodologies such as Eco-indicator 99 and IPCC 2007 as well as a detailed

comparison of RMC production with that of PC.

1.2 Goals and novelty of the research

This research focused on two novel research areas that have not been investigated in detail or at all until now. The first research area was based on the enhancement of the carbonation process, mechanical performance, and strain-hardening and self-healing behaviors of RMC formulations through the investigation of various mix designs, introduction of different additives and RMC sources, and use of polyvinyl alcohol (PVA) fibers on the performance of RMC formulations. The final performance of the developed mixes was reported in terms of their porosity, density, isothermal calorimetry, workability, thermal conductivity, water sorptivity, compressive strength, tensile strength, crack healing efficiency, resonance frequency and microstructural development under various curing/healing conditions. The major controlling parameters investigated under different conditions in were the water, cement and aggregate contents, the introduction of AEA, PFA, GGBS, calcined dolomite and PVA fibers. The phase formations at the end of each curing period were characterized by x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) with energy dispersive X-ray spectroscopy (EDX) and thermogravimetric analysis (TGA). The findings of this study were novel as only a very limited number of studies have been reported on the influence of these parameters on the performance RMC mixes. The objectives of this research topic were:

1. Examination of the influence of mix design (i.e. water, cement and aggregates contents) and the introduction of additives (i.e. AEA, PFA and GGBS) on the porosity, density, strength gain, thermal conductivity, carbonation ability and microstructure development of RMC mixes.
2. Investigation of the influence of calcined dolomite as a new type of RMC source on the mechanical properties, carbonation ability and microstructure development of RMC mixes under different curing conditions with varying temperature and relative humidity.

3. Investigation of the influence of PVA fibers on the strain-hardening and self-healing behaviours of RMC mixes under various curing (healing) conditions.
4. Characterization of the final products from a performance standpoint and identification of optimum mix designs in terms of performance and sustainability.

The second research area involved the sustainability assessment of the production of RMC. The goal of this study was to investigate the environmental impacts of RMC production. This was then completed with a comparison of the outcomes with PC. This study led to the evaluation of the relevant environmental aspects involved during the production of RMC ranging from the acquisition of raw materials to the packaging of the final product. The obtained results were compared with those of PC production via a thoroughly performed LCA. Different impact assessment methods including Eco-indicator 99 are used to investigate and identify the key environmental impact categories such as climate change and human health. The findings of this study were novel as the environmental impacts of RMC production were not studied in detail until now. The objectives of this research topic were:

1. Assessment of the environmental impact of RMC production within the construction industry.
2. Evaluation and comparison of the impact categories (e.g. climate change) and damage categories (e.g. human health) of RMC and PC production.
3. Utilization of a sensitivity analysis through scenario modelling for the evaluation of the accuracy of the assumptions and estimation of the influence of the parameters used on the final LCA outcomes.

1.3 Layout of the report

This report incorporates 7 chapters in total, the details of which are provided below:

Chapter 1 introduces the general research area, provides background information on the two research topics investigated in this study and presents their main goals and objectives.

Chapter 2 provides a detailed literature review on the production and properties of RMC, its use in various cement-based blends and the different parameters affecting the performance and environmental impacts of the developed formulations, including the influence of various types of additives.

Chapter 3 presents information on the materials, sample preparation methods and experimental and assessment procedures used in this study.

Chapter 4 presents and discusses the results obtained on the enhancement of carbon sequestration and mechanical performance of RMC formulations through the variation of mix design (i.e. water, cement and aggregates contents); and introduction of several additives (i.e. AEA, PFA and GGBS).

Chapter 5 presents and discusses the results obtained on the enhancement of carbon sequestration, mechanical performance and environmental impacts of RMC formulations through the investigation of calcined dolomite as a new type of RMC source under different curing conditions.

Chapter 6 presents and discusses the results on the strain-hardening and self-healing behaviors of RMC formulations involving the use of PVA fibers under different healing conditions.

Chapter 7 presents and discusses the results obtained on the life cycle assessment of RMC production and application in comparison to PC.

Chapter 8 highlights the conclusions reached and presents a guideline of future work.

Chapter 2 LITERATURE REVIEW

2.1 Cement sustainability

Owing to its excellent mechanical performance, abundant resources, availability of its raw materials on a global scale and simple production process, Portland cement (PC) is the most popular and widely used construction material in the world with an annual global production of over 4 billion tonnes (Portland Cement Association 2015, US Geological Survey 2015). Production of PC results in 5-10% of global anthropogenic CO₂ emissions (Olivier, Peters et al. 2012) and a large amount of resource consumption. The amount of energy consumed annually during this process is about 2780–3050 terawatt hours, accounting for ~2–3% of global primary energy use (Juenger, Winnefeld et al. 2011). Three main initiatives are currently being practiced to alleviate this problem: (i) partial cement replacements with low carbon materials, industrial by-products and wastes, (ii) improvement of the overall energy efficiency with the use of alternative raw materials, renewable energy sources, and low-energy production methods and (iii) development of new cement formulations with potentially lower carbon footprints; an example of which is reactive magnesium oxide (MgO) cement (RMC).

RMC is produced at lower calcination temperatures than PC (700-1000 vs. 1450 °C) (Green 1983, Birchall, Rocha et al. 2000), can sequester CO₂ during setting and gain strength accordingly, improve the durability of the formulations it is included in due to its high resistance in aggressive environments, enable utilization of waste and industrial by-products due to the low sensitivity of its hydration products to impurities and have the potential to be fully recycled when RMC is used as the only binder. Apart from the calcination of magnesite, MgO can be synthesized from seawater or brine obtained as a waste at the end of the desalination process (Barba, Brandani et al. 1980, Green 1983, Bocanegra-Bernal 2002).

2.2 Classification and properties of MgO

MgO is classified under four categories depending on the calcination temperature used during its production via the dry process route. All the different grades and properties of MgO currently used in different industries are presented in Table 2.1 (BREF 2010, Unluer and Al-Tabbaa 2015). RMC is produced at lower calcination temperatures than PC (~800 vs. 1450°C). Different from dead-burned MgO, whose utilization as a cement binder can cause large and localized volume expansions that can create cracking in the hardened cement due to its delayed hydration, RMC undergoes hydration at a similar rate as PC, thus avoiding any compatibility issues (Vandeperre, Liska et al. 2008).

Table 2.1 Different grades and properties of MgO (Unluer and Al-Tabbaa 2015)

Grade	Calcination temperature (°C)	Reactivity	Specific Surface Area (m ² /g)	Crystallinity
Light-burned (reactive, caustic calcined)	700-1000	Highest	>20	Lowest
Hard-burned	1000-1400	Lower	1-20	Higher
Dead-burned (periclase)	1400-2000	Even lower	<1	Even higher
Fused	> 2800	Lowest	0.01-0.1	Highest

There are several benefits when RMC is included as a cement binder: (i) ability to carbonate and gain strength accordingly via the formation of hydrated magnesium carbonates (HMCs); (ii) favorable fire resistance due to its low thermal conductivity (Shand 2006); (iii) great durability performance under aggressive conditions as due to the higher resistance of the hydration and carbonation products in aggressive environments where reinforcement is not present; (iv) lower sensitivity to impurities enabling the utilization of large quantities of waste and industrial by-products; and (v) potential to be fully recycled at the end of lifetime when used as the sole binder as its carbonates decompose back to MgO when heated thereby enabling the incorporation of industrial by-products (Liska 2010, Mo and Panesar 2012, Unluer 2012, Mo and Panesar 2013, Unluer and Al-Tabbaa 2014).

2.3 Production of MgO

MgO is found in minerals such as magnesite (MgCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$). Magnesium is also the third most abundant element in seawater (Shand 2006). MgO is obtained by two main methods:

- (i) Calcination of magnesia-based minerals (e.g. magnesite or dolomite)
- (ii) Synthetically from brine or seawater

A majority of the MgO utilized today is currently produced from the calcination of MgCO_3 , which is found in two physical forms: (i) cryptocrystalline or amorphous magnesite; and (ii) macrocrystalline magnesite (Cardarelli 2008). Pure magnesite contains 47.6% MgO and 52.4% CO_2 by weight. Small amounts of calcite (CaCO_3) and siderite (FeCO_3) can also be detected in natural magnesite, which can coexist with dolomite generally found in the form of sedimentary rocks (Alderman and Von der Borch 1961, Cardarelli 2008, BREF 2010). Raw magnesite is widely used in ceramics, surface coatings, landscaping and flame retardants (Cardarelli 2008).

Calcination of MgCO_3 to form RMC occurs at temperatures between 700-1000°C and is an endothermic reaction (i.e. total energy requirement of ~ 2415 kJ/kg), as indicated in Equation 2.1. RMC has a very high specific surface area (SSA) and reactivity. The lower calcination temperatures used in the production of RMC compared to PC (~800 vs. 1450°C) allows the use of alternative fuels with relatively low heating values. When compared to the calcination of MgCO_3 , the synthetic process involving the production of MgO from MgCl_2 rich brine or seawater through the wet process route is much more complex. The higher energy requirements and the associated cost of this production route can be justified by the higher purity (> 97%) of the final MgO (Cardarelli 2008, Ferrini, De Vito et al. 2009, BREF 2010, Hassan 2014), which may be desirable in certain applications within the pharmaceutical or food industries.

It is estimated that about 14 million tonnes/year of MgO is produced worldwide. For comparison, production of PC exceeds 4.1 billion tonnes/year (Portal 2016). The 3.7 billion tonnes of magnesite reserves in China account for ~29% of the world's total reserves (Li, Zhang et al. 2015). Although magnesite resources are widely available, 75% of the global magnesite production is from China, North Korea, Slovakia, Turkey, Russia, Australia and India (Shand 2006). The total production of MgO from magnesite is ~8.5 million tonnes/year (USGS 2012) and the leading producers are China, Russia and Turkey, who are responsible for 49%, 12% and 6% of total MgO production, respectively (Vandeperre, Liska et al. 2008). Fig. 2.1 presents the worldwide sources of magnesite and countries where a majority of MgO production takes place. China has the largest magnesite reserves in the world and is the largest producer, consumer and exporter of MgO. Calcination of magnesite usually takes place in shaft or tunnel kilns. Low quality control measures practiced in China result in inconsistent calcination conditions

(temperature and residence time), which can cause large temperature variations at different locations within the kiln, producing MgO with heterogeneous reactivity.

Fig. 2.1 Worldwide sources of magnesite and countries where a majority of MgO production takes place (AG 2006, EUROMINES 2006)

2.4 Carbonation of concrete

Mineral carbonation is a naturally occurring process in alkaline earth metals (e.g. Mg and Ca) and in Ca/Mg silicate rocks such as olivine and serpentine, which can react with atmospheric CO₂ to produce stable Ca/Mg-bearing carbonate. The corresponding reaction is shown below in Equation 2.2 (Seifritz 1990, Sipilä, Teir et al. 2008).

The carbonation of PC-based concrete applications can be described with a chemical reaction between the CO₂ present in air and the calcium in the pore solution of concrete in equilibrium with the hydration of cement (Van Balen 2005, Hyvert, Sellier et al. 2010), as shown in Equations 2.3-2.5 (Atiş 2003, Chang and Chen 2006, Han, Namkung et al. 2015). Carbonation results in

the decalcification of the hydrated cement paste via the reaction between Ca-bearing phases in cement and CO₂ from air, which penetrates into the pore network (Papadakis, Vayenas et al. 1991, Bradshaw and Cook 2001).

The first stage of carbonation involves the dissolving of CO₂ in the pore solution to form carbonic acid, which then reacts with portlandite (Ca(OH)₂) and calcium silicate hydrate (C-S-H) to form calcium carbonate (calcite, CaCO₃), as shown in Equations 2.6-2.8. Some studies have reported that carbonation of C-S-H begins immediately after a vast majority of Ca(OH)₂ reacts with CO₂ (Groves, Rodway et al. 1990, Peter, Muntean et al. 2008) and results in microstructural changes (e.g. porosity, pore size distribution, connectivity, specific surface area) (Rostami, Shao et al. 2012, Morandau, Thiery et al. 2014). Others have shown that carbonation of Ca(OH)₂ and C-S-H starts at the same time, and the initial reaction rate is quite similar, however, while C-S-H is still undergoing carbonation, carbonation rate of Ca(OH)₂ reduces and finally ceases as it becomes increasingly less accessible for carbonation (Villain, Thiery et al. 2007, Morandau, Thiery et al. 2014).

A reduction in strength can be observed with the carbonation of PC mixes due to the transformation of C-S-H into CaCO₃ and a highly porous and

hydrous form of silica (Taylor 1997, Liska and Al-Tabbaa 2009). As carbonation proceeds, micro-cracks start forming in the carbonated areas, increasing the permeability and decreasing the strength of concrete (Rimmelé, Barlet-Gouédard et al. 2008, Fabbri, Corvisier et al. 2009). Therefore carbonation is not a desirable reaction for maintaining the mechanical performance and durability of PC mixes. Fig. 2.2 presents the steps involved in the carbonation of PC mixes (Shafique, Walton et al. 1998, Bertos, Simons et al. 2004)

Fig. 2.2 Steps involved in the carbonation of PC mixes (Shafique, Walton et al. 1998, Bertos, Simons et al. 2004)

On the other hand, RMC-based formulations gain strength by carbonation as a result of the formation of hydrated magnesium carbonates (HMCs). The mechanism behind this strength development is based on: (i) the reduction in porosity as carbonation reactions are expansive processes that reduce the overall pore volume (i.e. the formation of HMCs causes significant expansion and increases the solid volume by a factor of 1.8-3.1); and (ii) microstructure evolution as the morphology and the binding strength of the carbonate crystals contribute to the network structure. The changes in the performance and microstructure due to the hydration and carbonation of MgO cements

over a range of compositions have been previously studied (Liska, Vandeperre et al. 2006, Vandeperre and Al-Tabbaa 2007, Vandeperre, Liska et al. 2007, Vandeperre, Liska et al. 2008, Vandeperre, Liska et al. 2008). The main hydration product of RMC is magnesium hydroxide (brucite, $\text{Mg}(\text{OH})_2$) which forms at an early age compatible with the hydration of PC, thereby eliminating any late expansion problems usually experienced with dead-burnt MgO (Wang 2002, Vandeperre, Liska et al. 2008, Vandeperre, Liska et al. 2008). Brucite is ineffective as a binder as it does not make a major contribution to strength development by itself. This leads to a reduction in early age strength and stiffness when PC is replaced with MgO (Vandeperre, Liska et al. 2008). Therefore, the mechanical properties of MgO-based binders are not comparable with PC under ambient curing conditions (Li 2013). However, in the presence of sufficient water and accelerated carbonation conditions, brucite reacts with CO_2 , leading to the formation of a range of HMCs such as 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 ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$), artinite ($\text{Mg}_2\text{CO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$) and magnesium calcite ($(\text{Ca},\text{Mg})\text{CO}_3$) (Vandeperre, Liska et al. 2008, Mo and Panesar 2012, Mo and Panesar 2013, Panesar and Mo 2013, Unluer and Al-Tabbaa 2013). Concrete blends containing 4-10% MgO as the only binder along with 90-96% aggregates gain compressive strengths 2-3 times greater than corresponding PC mixes, mainly owing to the formation of HMCs (Unluer 2012). The microstructures of these carbonates, which are the main sources of strength, are shown in Fig. 2.3.

Fig. 2.3 Microstructure of typical HMCs: (a) nesquehonite (Ferrini, De Vito et al. 2009), (b) dypingite (Power, Wilson et al. 2007), (c) hydromagnesite (Teir, Kuusik et al. 2007) (d) artinite (Gruppo 2003), and (e) magnesium calcite (Mo and Panesar 2012, Mo and Panesar 2013, Panesar and Mo 2013)

The hydration and carbonation of MgO cements are demonstrated by Equations 2.9-2.13. Similar to PC mixes, the carbonation of MgO mixes can

be summarized in 6 main steps: (i) Diffusion of CO₂ into the unsaturated pore network, (ii) penetration of CO₂ into the liquid pore membranes, (iii) dissolution of CO₂ in the pore water, (iv) formation of carbonic acid (H₂CO₃) in the pore solution, (v) ionization of H₂CO₃ into H⁺ and CO₃²⁻, (vi) leaching of Mg²⁺ from the dissolution of Mg(OH)₂ and (vii) formation and precipitation of HMCs due to the reaction between Mg²⁺ and CO₃²⁻ (Shafique, Walton et al. 1998, Bertos, Simons et al. 2004).

Understanding the factors that influence the carbonation process of MgO cement-based concrete mixes is necessary to increase the degree and rate of carbonation (Van Balen 2005, Vandeperre and Al-Tabbaa 2007, Liska and Al-Tabbaa 2008, Park 2008, Liska and Al-Tabbaa 2009, Unluer and Al-Tabbaa 2014). Three main factors control the rate and degree of carbonation as well as the associated strength development: (i) Mix design (i.e. cement and aggregate components, water content and particle packing arrangement of different aggregate profiles) (Liska and Al-Tabbaa 2009, Unluer and Al-Tabbaa 2012, Jin, Gu et al. 2013, Jin, Gu et al. 2015) (ii) curing conditions (curing time, CO₂ concentration and pressure, relative humidity (RH), temperature and wet/dry cycling frequency) (Mo and Panesar 2012, Unluer and Al-Tabbaa 2014), and (iii) presence of additives (supplementary cementitious materials (SCMs), admixtures, cement and aggregate replacements) (Vandeperre, Liska et al. 2008, Panesar and Mo 2013, Unluer and Al-Tabbaa 2013, Unluer and Al-Tabbaa 2015).

Fig. 2.4 summarizes the main factors influencing the carbonation of concrete mixes in general as the diffusivity of CO₂ and its reactivity with concrete. The former is determined by curing conditions and the pore structure of concrete, whereas the binder content and properties along with the extent of hydration influence the latter. The reaction kinetics involving the diffusion of CO₂ into the cement matrix and its interaction with the available hydration products is of interest in this study, which focuses on the role of carbonation in the strength gain of MgO-based concrete formulations.

Fig. 2.4 Factors controlling concrete carbonation (Pu and Unluer 2016)

The amount, distribution and interconnectivity of pores within concrete mixes influence the ease of CO₂ penetration into the cement matrix. Earlier studies on the carbonation of PC-based concrete have reported the influence of porosity on the final mechanical performance and durability of concrete mixes (Ngala and Page 1997, Ishida and Maekawa 2000, Johannesson and Utgenannt 2001, Song and Kwon 2007, Brameshuber 2008, Frías and Goñi 2013). Hydration products fill the available space between cement particles, decreasing the overall permeability and hindering the diffusion of CO₂ further into the system (Ewertson and Petersson 1993, Liska and Al-Tabbaa 2008, Mo and Panesar 2012, Junior, Toledo Filho et al. 2015). While a high initial

porosity results in low strengths, a certain amount of porosity is needed for continuous carbonation. The transformation of hydration products (Ca(OH)_2 or Mg(OH)_2) into carbonation products (CaCO_3 or HMCs) slows down the ingress of further CO_2 within the available pore system. An ideal MgO-based mixture that relies on carbonation for strength gain should not only be permeable enough to allow for significant CO_2 diffusion but also form a strong network to provide sufficient physical strength. Concrete formulations with porous structures were used in this study to facilitate the diffusion of CO_2 within the pore system. Carbonation efficiency can also be improved by raising the temperature as higher reaction temperatures enable a faster rate of hydration and CO_2 diffusion into the pore system (Ukwattage, Ranjith et al. 2014, Han, Im et al. 2015). This is because gas molecules possess larger motion energies and demonstrate more frequent collision movements when subjected to higher temperatures, leading to faster reaction and diffusion rates. Other factors influencing the progress of carbonation reaction include RH (Russell, Basheer et al. 2001, El-Turki, Ball et al. 2007), CO_2 concentration (Vandeperre and Al-Tabbaa 2007, Castellote, Fernandez et al. 2009), and CO_2 flow rate (Jo, Kim et al. 2012).

As carbonation relies on the ingress of CO_2 into the concrete pore system, the concentration and pressure of CO_2 in the curing environment also control the carbonation rate. An obvious improvement in strength, density and stiffness of MgO cement formulations is achieved under high CO_2 concentration curing (Neville 1995, Chi, Huang et al. 2002). This can be explained by the increase of solid volume (i.e. by a factor of 1.8-3.1) and reduction of porosity associated with the expansive formation of various HMCs or magnesian calcite ($(\text{Ca,Mg})\text{CO}_3$) with a high micro-hardness (Vandeperre and Al-Tabbaa 2007, Mo and Panesar 2012, Mo and Panesar 2013). Another source of strength gain is the microstructural evolution as the morphology and the binding strength of the carbonate crystals contribute to the network structure. HMCs contributes to the microstructural strength of the cement formulations due to their strong, fibrous, acicular or otherwise

elongated nature via the interlocking effects occurring between the crystals. Fibrous and needle-like crystal growths provided by HMCs are more beneficial than rounded or tabular crystals due to the formation of 3D structures. Nesquehonite is prismatic and forms star-like clusters, whereas dypingite and hydromagnesite are comprised of rounded rosette-like crystals. The elongated morphology of nesquehonite reduces porosity and enhances stiffness by raising the solid volume by a factor of 2.3 upon its conversion from brucite. The overall performance is determined by the compact and interlocked network-like structure provided by interconnected and well developed crystals (De Silva, Bucea et al. 2006). A further enhancement is provided via the formation of bulk “micro-aggregate” due to localized carbonation, which also contributes to the creation of a dense matrix (Mo and Panesar 2012). Alternatively, brucite is detected in natural curing or uncarbonated MgO blends (Unluer and Al-Tabbaa 2013).

MgO mixes subjected to accelerated carbonation curing under a CO₂ concentration of 5-20% can achieve up to 100% carbonation in as early as 14 days, depending on the mix design. Although carbonation process can be accelerated by increasing the concentration of CO₂, there seems to be a limit at a CO₂ concentration of ~10%. Further increases in the CO₂ concentration do not have a significant influence on the carbonation degree as other factors limit the diffusion of CO₂ within the samples beyond this point. Previous studies have reported that CO₂ concentrations as low as 5% resulted in blocks with a 1-day strength higher than 7 MPa (Unluer and Al-Tabbaa 2014), which meets the strength requirement of commercial concrete blocks (British Standard-771-4 2011).

The formation of HMCs in carbonated MgO systems depends on the reactivity and impurities present within MgO, along with the water content, temperature and CO₂ concentration they are exposed to. An increase in temperature leads to the transformation of carbonates into those that are less hydrated than

others, whereas a change in CO₂ concentration also results in the formation of different phases. Other parameters such as water activity and pH also influence the formation of different HMCs. The co-existence of several HMCs such as nesquehonite, hydromagnesite and dypingite has been observed in previous studies that have looked into the microstructure and mechanical performance of carbonated MgO systems (Liska and Al-Tabbaa 2009, Liska and Al-Tabbaa 2012, Liska, Al-Tabbaa et al. 2012, Unluer 2012, Yi, Lu et al. 2015). The formation of a dense layer of nesquehonite along with hydromagnesite and dypingite generally contributes to the strength development in blends where MgO is used as the main binder.

Optimization of the use of MgO in cement blends requires a deep understanding of the effect of parameters such as blend composition (e.g. cement content, aggregates content and water/binder ratio), curing conditions (e.g. CO₂ concentration and RH and the utilization of additives and admixtures on the properties of the final products. Thereby, this study focuses on the investigation of these major parameters on the performance of MgO cement mixes. The obtained results build on the existing knowledge on MgO cements and aim to reveal the carbonation mechanism of RMC-based concrete mixes by providing a comparison with corresponding PC mixes.

2.5 Influence of mix design and use of additives on the performance of concrete

2.5.1 Adjustment of water to cement ratio and cement and aggregate contents

Similar to PC mixes, the initial water content plays an important role in the strength development of RMC mixes as water provides a medium for the hydration and carbonation reactions (Unluer and Al-Tabbaa 2014, Pu and Unluer 2016). Increasing the water content of concrete mixes can increase the capillary porosity and improve the interconnectivity of voids, thereby

enhancing the carbonation process (Houst and Wittmann 1994, Wong, Pappas et al. 2011). Meanwhile, the presence of excess water can inhibit the diffusion of CO₂ within the pore system, thereby slowing down carbonation. The optimization of the water content is critical as low water/cement (w/c) ratios can lead to the poor compaction and crumbling of RMC mixes, whereas high w/c ratios can reduce the CO₂ diffusivity and therefore hinder the formation of HMCs and associated strength development (Unluer and Al-Tabbaa 2014).

Another factor that can influence the strength development of RMC-based concrete mixes is the cement content (i.e. aggregate/cement ratio) (Erntroy and Shacklock 1954, Singh 1958). As the carbonation of RMC mixes involves a series of reactions within the MgO-CO₂-H₂O system, an increase in the cement content can potentially lead to an increase in the amount of final hydrate and carbonate phases. However, this can also lead to the decrease of initial porosity as the fine cement particles fill in the available pores between the coarse aggregates. While this would lead to increased strength in PC mixes that rely on the hydration process for strength gain, the provision of a sufficiently high porosity within the initial mix design via the use of a high aggregate content is essential for the continuation of the carbonation reaction within RMC mixes. Therefore, the optimization of the aggregate/cement ratio is important for the enhancement of gas diffusivity and permeability (Buenfeld and Okundi 1998). Along with the aggregate/cement ratio, the amount and the saturation level of aggregates can determine the effective water content within a mix. Increasing the amount of aggregates can alleviate shrinkage and bleeding and therefore improve the bond between the aggregates and cement paste (Neville 1995), whereas high aggregate contents eventually lead to lowered strengths due to the corresponding reductions in the cement content (Stock, Hannant et al. 1979).

2.5.2 Introduction of air-entrained agents (AEA)

The penetrability and diffusivity of CO₂ into the pore network is also dependent on the mix porosity (Johnson 2000). Lower porosities prohibit the diffusivity of the CO₂ into the solid matrix, therefore reducing the formation of carbonate phases and leading to lower strengths in RMC mixes. It is therefore important to design mixes that can enable the continuous diffusion of CO₂ through a well-connected pore network. This can be enabled via the generation of air voids in addition to the gel and capillary pores via the introduction of air-entrained agents (AEA), which are regarded as one of the most crucial technological breakthroughs in construction materials within the last century (Du and Folliard 2005). AEA are generally included in fresh cement blends to increase workability and consistency, mitigate bleeding and segregation and improve durability (Du and Folliard 2005, Lamond and Pielert 2006, Pigeon and Pleau 2010). Another benefit of AEA is the reduction of thermal conductivity due to the increased air content that is resistant to heat flow (Sengul, Azizi et al. 2011, Kim, Jeon et al. 2012). The main drawback of air entrainment is its adverse effect on compressive strength due to the increased porosity and associated reduction of the overall density. However, the reduction in strength can be compensated by the water-reducing effect of AEA.

Entrained voids can have larger sizes than typical pores readily present in cement mixes (Neville 1995). The formation and stability of the generated air bubbles are directly influenced by the rheological properties of the cement paste. Some studies (Neville 1995, Du and Folliard 2005) have reported high viscosities and yield stresses to be favourable for the formation of air bubbles enabled by the introduction of AEA, whereas others (Tattersall 1976) suggested that high viscosities can act as an energy barrier and slow down the formation of bubbles. Although they may seem isolated, the entrained voids can be interconnected by the capillary pores within the pore structure (Wong, Pappas et al. 2011), thereby providing a continuous path for the

diffusion of CO₂. The air void-paste interface is similar to the interfacial transition zone (ITZ) generated between aggregates and paste in terms of its lower content of hydration products and larger porosity than the rest of the matrix, enabling a permeable network for CO₂ ingress. An up to 2-3 fold increase in gas permeability and diffusivity was reported via the introduction of AEA within concrete mixes despite the lower water contents (Wong, Pappas et al. 2011), whereas other studies (Cultrone, Sebastian et al. 2005) claimed a lack of change in the carbonation degree of PC-lime blends, albeit a reduction in drying cracks and changes in texture via the formation of round pores.

Air-entrained agents are recommended for nearly all types of concrete, especially when concrete are subjected to freeze-thaw cycles (Wong, Pappas et al. 2011). A number of studies indicated that many factors influence the content and dimension of the entrained air voids such as the type and dosage of air-entraining agent, mix design and mixing sequence. These issues and concepts concerning freeze-thaw damage and the advantages of the inclusion of the air entrainment have been investigated in several studies (Wong, Pappas et al. 2011, Mayercsik, Vandamme et al. 2016).

2.5.3 Introduction of PFA and GGBS

Various performance of binders containing PFA and GGBS can be achieved based on the materials used and curing conditions, and there are two mechanisms accounting for the performance variance of binders under carbonation. The first could be related with the pozzolanic effect and the alkaline substances are consumed, decreasing the pH and facilitating carbonation (Sisomphon and Franke 2007, Torgal, Miraldo et al. 2012), and another could be attributed to the formation of hydration phases, which decreases porosity and inhibits carbonation (Aprianti, Shafigh et al. 2015).

The hydration mechanism of SCMs such as PFA and GGBS in the presence

of RMC has been reported by previous studies (Vandeperre and Al-Tabbaa 2007, Vandeperre, Liska et al. 2007, Vandeperre, Liska et al. 2008, Jin, Gu et al. 2013, Li 2013), where the ability of MgO to activate SCMs and enable the formation of calcium silicate hydrate (C-S-H), magnesium silicate hydrate (M-S-H) and hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4(\text{H}_2\text{O})$) by providing the necessary pH for the increased solubility and dissolution of glassy phases within SCMs was demonstrated. Activation of GGBS by MgO yielded higher strengths than its activation by hydrated lime due to the formation of a higher content of hydrotalcite in the former system (Yi, Liska et al. 2014). The main reaction products of RMC-GGBS systems were reported as C-S-H and hydrotalcite (Jin, Gu et al. 2013), whereas the use of high PFA contents within RMC-PFA systems led to strength gain via the formation of M-S-H and hydrotalcite (Vandeperre and Al-Tabbaa 2007, Vandeperre, Liska et al. 2008, Yi, Liska et al. 2014, Yi, Liska et al. 2014).

While PFA and GGBS have limited carbonation capabilities by themselves, their use in cement mixes with varying compositions has revealed their ability to react with CO_2 in alkaline solutions (He, Yu et al. 2013, Wee 2013, Siriwardena and Peethamparan 2015). Several studies (Liska, Vandeperre et al. 2008, Mo and Panesar 2013) showed that RMC samples involving the use of PC with PFA or GGBS achieved superior performances than corresponding PC samples under carbonation. This was attributed to the higher carbonation degrees of these samples enabled by their permeable structures that facilitated the diffusion of CO_2 through the pore network. The carbonation process led to the production of HMCs and/or magnesium calcite (Mg-CaCO_3), which improved the morphology and facilitated carbonate agglomeration, leading to dense and interconnected microstructures (Vandeperre and Al-Tabbaa 2007, Vandeperre, Liska et al. 2008, Vandeperre, Liska et al. 2008, Panesar and Mo 2013, Yi, Liska et al. 2014, Yi, Liska et al. 2014, Mo, Zhang et al. 2016). Further studies on formulations involving the use of PC, RMC and PFA indicated a reduction in their CO_2 emissions owing to the carbonation of Mg- and Ca-phases when cured under

pressurized CO₂ with a concentration of ~99.9% and pressure of 0.1-1.0 MPa (Mo, Zhang et al. 2016). When subjected to CO₂ curing under high pressures, these samples demonstrated lower net CO₂ emissions than corresponding PC samples, during which an increase in CO₂ pressure enabled a higher CO₂ uptake as well as early compressive strength gain (Mo and Panesar 2012, Mo and Panesar 2013, Panesar and Mo 2013, Mo, Zhang et al. 2016).

2.6 Introduction of calcined dolomite

Dolomite (CaMg(CO₃)₂), composed of magnesium and calcium carbonate, is a naturally occurring mineral widely available globally. Its main reserves are found in North America, former Soviet Union, Far East, Middle East and Africa (Warren 2000). The theoretical composition of dolomite includes 22% MgO, 30% CaO and 48% CO₂. The mineral form of dolomite is typically found with variable contents of calcite. Other metallic ions within dolomite include manganese, lead, zinc, cobalt, nickel and strontium (Hossain, Dlugogorski et al. 2011). Dolomite is utilized in multiple industries including the production of concrete, cement, glass, paper and fertilizers, as well as the metallurgy and pharmaceutical industries (Makó 2007). Sorbents made of dolomite are used to reduce the emissions of various pollutants including nitrogen, oxides of sulfur and carbon, fluoride and hydrogen chloride under low temperatures (Hartman, Trnka et al. 1996, Hossain, Dlugogorski et al. 2011, Przepiórski, Czyżewski et al. 2013). The performance of dolomite within these applications are determined by its thermodynamic, structural and physicochemical properties.

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 2.14; and (ii) decomposition of calcite at > 700 °C, as shown in Equation 2.15 (P.G. Caceres 1997, Maitra, Choudhury et al. 2005, Sasaki, Qiu et al. 2013). The exact decomposition patterns depend on the properties of the starting material (e.g. composition), calcination conditions

(e.g. temperature and residence time), presence of impurities, and use of additives (e.g. sodium chloride). Varying the calcination conditions of dolomite can lead to final products with different chemical compositions mainly including MgO, MgCO₃, CaO and CaCO₃. Blends involving the use of dolomite calcined under different conditions has found various applications in the cement industry as binders, aggregates and expansive additives (Galí, Ayora et al. 2001, Díaz, Torrecillas et al. 2005, Barbhuiya 2011, Gu, Jin et al. 2014, Yang, Ryu et al. 2014, Liu, Wang et al. 2015, Verian, Panchmatia et al. 2015). Furthermore, dolomite has been used as an activator in alkali activated binders (Gu, Jin et al. 2014, Gu, Jin et al. 2016). When compared to the most common alkaline activators (e.g. sodium silicate, sodium hydroxide, sodium carbonate and potassium hydroxide), which are generally not naturally available and require energy intensive production processes, CaO and MgO extracted from dolomite can present more economical alternatives. Recent studies (Gu, Jin et al. 2014) reported that calcined dolomite is more effective in accelerating the hydration of slag than reactive MgO by itself, albeit being slower than PC (Shi, Roy et al. 2006, Rashad 2013).

One way of extracting Mg from dolomite is through the Pidgeon process, which involves the initial calcination of the raw material (i.e. dolomite), followed by the introduction of ferrosilicon for the separation of Mg and Ca, which are the main phases obtained when dolomite is calcined (Ramakrishnan and Koltun 2004). Dolomite can also be used as a starting material in the production of magnesium oxychloride cement, which also leads to the production of high-purity CaCO₃ and CO₂ (Altiner and Yildirim 2017, Altiner and Yildirim 2017). Other studies on the use of dolomite have reported the properties of an alkali-activated cement system involving a mix of dolomite and bentonite subjected to calcination under high temperatures

(~1100-1200 °C) (Peng, Wang et al. 2017). Another study (Szybalski and Nocuń-Wczelik 2015) investigated the role of dolomite on the hydration of cement, where dolomite was added as an active ingredient or as a cement replacement at low dosages. Half-burnt dolomite, composed of MgO and CaCO₃, has also been used as a supplementary cementitious material (SCM) to partially replace PC. The replacement of up to 20-25% PC by half-burnt dolomite was reported to retain compressive strength at 28 days, while the maximum strength gain was observed at a replacement level of around 10-15%. Within these mixes, the particle size distribution and accessibility of MgO to water greatly affected the reactivity of half-burnt dolomite used as a SCM (Jauffret and Glasser 2016). Other than its use as an additive within the binder content, raw dolomite extracted as a natural resource can also be used as a coarse aggregate within concrete mixes (Prokopski and Halbiniak 2000).

2.7 Development of strain-hardening composites with the ability to undergo self-healing

2.7.1 Strain-hardening behavior

The inclusion of a small amount of short polymeric fibers has been proven to be very effective in eliminating the brittleness and enhancing the tensile ductility of PC-based composites (Brandt 2008). One of the successful derivatives involving the use of fibers is engineered cementitious composites (ECC), which adopt polymeric fibers at a fraction of typically ~2% by volume. Unlike the strain-softening conventional PC, ECC demonstrate strain-hardening behavior as their tensile stress continues to increase even in the presence of cracks. ECC samples can achieve a tensile ductility of 1-5%, enabled by the formation of multiple fine cracks (< 100 µm) with very small spacing (1-5 mm) (Li, Mishra et al. 1995, Li, Wang et al. 2001, Yang, Yang et al. 2007). The tensile properties of ECC can be further tailored with micromechanics to achieve multiple attributes such as high impact resistance (Yang and Li 2012, Yang and Li 2014) and fatigue resistance (Qiu, Lim et al. 2016, Qiu and Yang 2016). Therefore, to increase the use of RMC without

relying on steel reinforcement, it is desirable to engage similar tensile strain-hardening behavior and high ductility within RMC-based formulations via the addition of short polymeric fibers.

While a desirable fiber dispersion is critical, it does not necessarily guarantee strain-hardening behavior or high ductility. As shown in Fig. 2.5, the hardened composites must satisfy the two strain-hardening criteria (Yang, Wang et al. 2008). Specifically, the complementary energy of the fiber-bridging curve, J_b' (i.e. the hatched area), must be larger than the crack tip toughness of the matrix, J_{tip} , as shown in Equation 2.16. Furthermore, the fiber-bridging strength, σ_0 (i.e. the curve peak), must be higher than the tensile cracking strength of matrix, σ_c , as shown in Equation 2.17.

$$J_{tip} \leq \sigma_0 \delta_0 - \int_0^{\delta_0} \sigma(\delta) d\delta \equiv J_b' \quad (2.16)$$

$$\sigma_c < \sigma_0 \quad (2.17)$$

Fig. 2.5 Illustration of the fiber-bridging constitutive law, showing the tensile stress-crack opening displacement $\sigma(\delta)$ curve and strain-hardening criteria (Yang, Wang et al. 2008)

The feasibility study of strain hardening magnesium oxychloride cement (MOC)-based composites has been reported in (Wei, Wang et al. 2018),

where it indicated that saturated crack pattern and small crack width could be observed when samples were subjected to tension, meanwhile, a tensile strain capacity up to 7% or even more could be observed. The evaluation of the environmental factors via the use of material sustainability indicators also indicated that reactive magnesia-based ECC mixes could lead to a reduction in the net CO₂ emissions of conventional ECC and concrete by 65% and 45% after 1 day of carbonation, respectively (Wu, Zhang et al. 2018).

2.7.2 Self-healing behavior

The mechanism of autogenous crack healing requires the cement matrix to be capable of continuously narrowing the crack width and restoring the original mechanical performance under certain environments without external intervention. The use of concrete capable of robust autogenous healing would greatly ease the maintenance of infrastructures (Li and Herbert 2012). The water-induced autogenous healing of PC-based concrete samples has been extensively studied (Li and Herbert 2012, Wu, Johannesson et al. 2012), where it was revealed that a controlled crack width was necessary for robust autogenous healing (Edvardsen 1999). Previous studies on fiber-reinforced PC-based composites (Yang, Lepech et al. 2009, Qiu, Tan et al. 2016) reported an allowable crack width of 50-100 µm, depending on the matrix mix design, for complete mechanical recovery; while no recovery was noticed at crack widths beyond 150 µm.

In addition to the control of crack width via the use of fiber reinforcement, expansive additives were also found to be effective in achieving robust healing (Ahn and Kishi 2010, Sisomphon, Copuroglu et al. 2012). One of these additive groups is MgO-type expansive agents (MEA), which have long been used for shrinkage compensation in mass construction. The effect of MEA on the autogenous healing of PC-based concrete has been reported in a number of recent studies (Qureshi and Al-Tabbaa 2014, Qureshi and Al-Tabbaa 2016, Sherir, Hossain et al. 2016, Sherir, Hossain et al. 2017). It was

found that both hard-burned and light-burned (i.e. reactive) MgO enhanced the crack sealing efficiency. Meanwhile, the inclusion of MgO in PC samples greatly reduced permeability of binders and the addition of MgO in the mixes increased the amounts of brucite, hydromagnesite, magnesian calcite, and M-S-H formation in healing phases within cracks (Qureshi, Kanellopoulos et al. 2018). More specifically, the use of reactive MgO in the presence of CO₂ led to the formation of HMCs that filled the cracks with a width of up to 500 µm (Qureshi and Al-Tabbaa 2016).

In terms of crack healing, microbial induced carbonate precipitation (MICP) has also been proposed as a novel approach for the protection and repair of cracks in cement-based composites (De Muynck, Cox et al. 2008). Within these structures, the use of urease-producing bacteria (UPB), such as bacillus sphaericus, to produce carbonate crystals between cracks has been proposed (De Muynck, Cox et al. 2008, De Muynck, Debrouwer et al. 2008, Van Tittelboom, De Belie et al. 2010). These bacteria enable the microbial deposition of CaCO₃ in a calcium-rich environment, in line with Equation 2.18 and 2.19.

Similarly the MICP process could be applied to other minerals such as iron (Ivanov, Chu et al. 2012) and magnesium, as shown in Equation 2.20 and 2.21, leading to the production of hydrated magnesium carbonates (HMCs):

Several factors contribute to the microbial mineralization of Ca- or Mg-carbonates, including the pH, the concentration of carbonate and calcium/magnesium ions, and the presence of nucleation sites. The first two factors are determined by the metabolism of the bacteria, while the nucleation sites are provided by the cell walls of the bacteria (Hammes and Verstraete 2002). The various physiological activities of bacteria can create an alkaline environment. This high pH environment and subsequent bacterial calcium metabolism are critical factors in MICP (Castanier, Métayer-Levrel et al. 1999, Ruan, Qiu et al. 2018). The basic mechanism behind the utilization of MICP to enhance autonomous healing of concrete involves the direct incorporation of UPB, nutrients (e.g. urease) and Ca-bearing phases (i.e. can be added externally) during concrete manufacturing (Dick, De Windt et al. 2006). However, UPB can generally not survive in harsh environments due to the highly alkaline environment within concrete and the stirring activity performed at a high speed during concrete mixing. Therefore, instead of directly subjecting the bacteria to extreme conditions, their encapsulation or immobilization in a protective carrier such as silica gel or polyurethane in macro capsules (Wang, Soens et al. 2014) and diatomaceous earth (Wang, De Belie et al. 2012) is necessary before incorporating them into concrete (Wang, Soens et al. 2014, Choi, Wang et al. 2017).

2.8 Life cycle assessment

Life cycle analysis (LCA) is an approach for assessing the environmental aspects related with a product in its entire life cycle (cradle to grave). And by indicating and quantifying energy and materials consumption and waste emission, LCA minimizes the environmental burdens associated with a product or a process correspondingly and enable the implementation of the Best Available Techniques (BAT) in product manufacturing (Curran 1994, Goedkoop, Schryver et al. 2010).

Several previous investigations reported the energy consumption and

environmental impacts associated with the production of magnesium and magnesium alloy production via the use of life cycle assessment (LCA) technique (Ramakrishnan and Koltun 2004, Kwon, Woo et al. 2015). In China, the smelting of dolomite is the main source of magnesium, whereas magnesite and magnesite masonry are primarily manufactured with magnesite. A number of studies have reported the energy conservation of the production of magnesite (main fused magnesite) refractory materials (Tong 2010, Li, Zhang et al. 2015). There are also some studies relating with the environmental impact of the magnesite industry such as soil contamination by magnesite dusts (Wu 2007) and groundwater contamination by magnesite mining (Bajtos and Bajtos 2004).

Li et al. (Li, Zhang et al. 2015) conducted a life-cycle assessment (LCA) of the different methods used in the production of fused MgO, starting from raw materials extraction to production. The authors reported that the production process itself makes the largest contribution to all the environmental categories investigated, which was attributed to the high power consumption during this process. Pan et al. (Pan, Zhang et al. 2002) investigated the utilization of rotary kilns with external heating and incorporation of CO₂ recycling technology in the production of caustic calcined (reactive) MgO and found that the amount of CO₂ and SO₂ emissions decreased with the implementation of these technologies. Yue et al. (Yue, Zhao et al. 2011) studied the use of a two-segment gas generator on a vertical kiln used for the production of light-burned (reactive) MgO and highlighted the effects of the utilization of dust remover, detarrer (tar and dust capture technology) and cleaner fuel sources, resulting in a 17.1% and 6.3% decrease in the amount of dust and SO₂ annually, respectively. Jing et al. (Jing and Xue 2016) indicated that priority should be placed on the direct carbon emission resulting from the production processes to cut down the overall carbon footprints of light calcined magnesite and sintered magnesite, whereas in terms of fused magnesite, the key point is to reduce the carbon footprint associated with electricity consumption by means of an improvement of the thermal efficiency

of heating furnaces.

Hassan (Hassan 2014) reported the theoretical energy demand of MgO produced via the dry (5.9 GJ / tonne of MgO) and wet (17.0 GJ / tonne of MgO) process routes to be larger than the production of PC from calcite (4.5 GJ / tonne of PC). The higher energy demand of MgO production is linked with (i) the higher total energy required for the acquisition of magnesite (~0.06 vs. 0.04 GJ/tonne required for limestone), (ii) the higher quantity of raw materials needed for MgO production (2.08 vs. 1.52 tonne for PC) and (iii) the higher work index value of magnesite than that of limestone (16.3 vs. 12.3 kWh/t). Therefore, although the calcination temperature of magnesite is lower, the energy required for the production of MgO is generally higher than PC. The total amount of CO₂ emitted during the production of MgO via the dry process was reported as 1.7 tonne/ tonne (t/t) of MgO (i.e. 1.1 t/t from the calcination of magnesite and 0.6 t/t from fuel combustion), while this value was reported as 1 t/t of PC produced (i.e. 0.67 t/t from the calcination of calcite and 0.33 t/t from fuel combustion). However, several studies have shown that the CO₂ emitted during the calcination of magnesite can be fully sequestered during the curing process of MgO cement-based construction products, which gain strength through the carbonation process (Liska and Al-Tabbaa 2009, Unluer and Al-Tabbaa 2013, Unluer and Al-Tabbaa 2014). This brings down the final net CO₂ emissions of MgO cements to ~0.5-0.6 t/t at no further cost, which is 40-50% lower than the total CO₂ emissions associated with PC production. This can be compared to the carbon capture and storage (CCS) technologies employed during PC production, which has a capture efficiency of 80-95% for post-combustion and 90-99% for oxy-combustion. While the use of CCS results in the reduction of CO₂ emissions, this comes at a high cost of around €41.2-53.8 /t CO₂ as well as the need for regular maintenance. Furthermore, this process can influence clinker properties (Carrasco-Maldonado, Spörl et al. 2016).

Chapter 3 MATERIALS AND EXPERIMENTAL PROCEDURES

This chapter provides the materials and experimental procedures used for the experimental work (i.e. related to the results on Chapters 4, 5 and 6) performed on RMC mixes.

3.1 Materials

3.1.1 Binders

(i) Reactive MgO cement (RMC) and Portland cement (PC)

The RMC used in sample preparation was calcined magnesite 92/200 supplied by Richard Baker Harrison Ltd. (United Kingdom) and International Scientific Ltd. (Singapore). The reactivity of RMC is assessed by citric test, where the reaction time of RMC from United Kingdom and Singapore is 859 and 1184 seconds respectively. The specific surface area of RMC from United Kingdom and Singapore is 9000 m²/kg and 7500 m²/kg according to the suppliers. The particle size distributions of MgO from Singapore and United Kingdom are shown in Fig. 3.1. The PC used in this study is obtained from Lafarge Singapore. Chemical composition and physical properties of RMC, PC are listed in Table 3.1.

Fig. 3.1. Particle size distributions of MgO from Singapore and United Kingdom

Table 3.1 Chemical composition and physical properties of RMC and PC

Cement binder	Chemical composition (wt.%)						
	MgO	SiO ₂	CaO	R ₂ O ₃	K ₂ O	Na ₂ O	LOI
RMC	>91.5	2.0	1.6	1.0	-	-	4.0
PC	0.9	20.9	66.2	10.0	0.5	0.08	1.1

(ii) PFA and GGBS

PFA (class F) and GGBS were provided by Bisley Asia (Singapore) and EnGro (Singapore), respectively. The chemical compositions of PFA and GGBS as provided by the suppliers are listed Table 3.2. The particle size distributions of PFA and GGBS are shown in Fig. 3.2.

Fig. 3.2 Particle size distributions of FA and GGBS

Table 3.2 Chemical compositions of the cementitious components used in sample preparation

	Chemical composition (wt.%)						
	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	K ₂ O	TiO ₂
PFA	0.8	1.2	58.6	4.7	30.4	1.5	2.0
GGBS	9.3	37.8	32.3	0.5	14.6	-	-

(iii) Calcined dolomite

The dolomite was obtained from International Scientific Ltd. (Singapore). Table 3.3 lists the chemical compositions of dolomite, as obtained from the suppliers. To produce the dolomite-based binder, dolomite was calcined at 700 °C, 800 °C (D800) and 900 °C (D900) in an electric furnace. Table 3.4 shows the chemical composition of D700, D800 and D900, which was obtained through XRD and Rietveld refinement method via the use of the software TOPAS. The calcination temperature was increased at 10 °C /min

increments to reach the target temperature, which was maintained for 3 hours. The powders were grinded for 10 minutes at a speed of 300 RPM.

Table 3.3 Chemical compositions of dolomite

Chemical Composition (wt.%)	Mg	Ca	Si	Fe	Na	K
Dolomite	27.4	70.0	0.2	-	1.9	0.5

Table 3.4 Chemical composition of D700, D800 and D900

Binder/Composition (wt.%)	MgO	CaO	CaCO ₃	CaMg(CO ₃)
D700	10.6	-	30.5	58.9
D800	27.6	0.3	71.7	0.4
D900	32.6	7.6	59.8	-

3.1.2 Aggregates

Saturated surface dry (SSD) gravel with a particle size of 4.7–9.5 mm was used to form the aggregate profile in the prepared concrete samples. The gravels were supplied by Buildmate Pte Ltd, Singapore.

3.1.3 Admixtures

(i) Air-entrained agent (AEA)

An air-entrained agent (AEA), EMAL 10N, containing sodium lauryl sulfate ($\text{NaC}_{12}\text{H}_{25}\text{SO}_4$) as its major component, was supplied by Megachem Singapore. The chemical structure used in this study are presented in Fig. 3.3.

Fig. 3.3 Chemical structure of sodium lauryl sulfate

(ii) Water reducer

Sodium hexametaphosphate ($\text{Na}(\text{PO}_3)_6$), acquired from VWR International Ltd. (Singapore), was added to some of the prepared formulations as a water reducer. Fig. 3.4 shows the chemical structure of sodium hexametaphosphate.

Fig. 3.4 Chemical structure of sodium hexametaphosphate

3.1.4 PVA fibers

Polyvinyl alcohol (PVA) fibers were obtained from Kuraray Ltd. (Japan) and Fig. 3.5 shows the PVA fibers used in this study. Table 3.5 shows the properties of the PVA fibers used in this study

Fig. 3.5 PVA fibers used in this study

Table 3.5 Properties of the PVA fibers used in this study

Length (mm)	Diameter (μm)	Density (kg/m^3)	Nominal tensile strength (MPa)	Surface oil content (%)
12	39	1300	1600	0

3.1.5 Urease producing bacteria (UPB)

Urease producing bacteria (UPB) used in the investigation of the self-healing behavior of RMC formulations was isolated from activated sludge obtained from a waste water treatment plant in Singapore and was identified as *Bacillus* species via genetic analysis. The mother culture was inoculated (1 ml/100 ml) and cultivated under aerobic sterile regimes. 10 g/L of ammonia chloride, 20 g/L of yeast extract and 100 μM of nickel chloride was included in the growth medium and the initial pH was fixed at 9. The bacterial cultivation was conducted at 25 ± 1 °C on an orbital shaker, at a shaking rate of 600 rpm. After 48 hours of cultivation, the bacteria culture was harvested. The urease activity, measured by a conductivity meter, was 10 U/ml (i.e. 1 U equates to 1 $\mu\text{-mole}$ of urea hydrolyzed per minute (Cheng, Cord-Ruwisch et al. 2013)), which was relatively high. Finally, the bacterial solution was stored at 4 °C prior to use. Two concentrations of urea solution, corresponding to 1 and 2 M, were prepared by dissolving solid urea in distilled water.

3.2 Mix compositions, sample preparation and curing/healing conditions

3.2.1 Investigation of influence of mix design and use of additives on the mechanical performance and carbon sequestration of RMC formulations

(i) Water, cement and aggregate contents (Chapter 4)

The standard consistency (SC) of RMC and PC were measured according to BS EN 196-3 as ~ 0.60 and 0.33, respectively (BSI 2016). This led to the

preparation of RMC and PC control samples containing 40% cement and 60% aggregates at w/c ratios of 0.60 and 0.33, respectively. Concrete samples were prepared by mixing the dry components first, followed with the addition of water to the dry mix. To study the effect of water content, RMC samples with two different w/c ratios corresponding to $SC \pm 8.3\%$ were prepared. The effect of cement content was studied by changing it by $\pm 12.5\%$. All the mix compositions containing RMC samples with different contents of water and cement content and PC samples using different curing conditions used in this study are listed in Table 3.6.

Table 3.6 Mix compositions of RMC samples with different contents of water and cement and PC samples with the curing of air, water and 10% CO₂

Mix	Mix composition (wt.%)			w/c ratio	Curing condition
	PC	RMC	Coarse aggregates		
PC-air	40	0	60	0.33	Air
PC-water					Water
M40-0.55	0	40	60	0.55	Accelerated CO ₂
M40-0.6				0.60	
M40-0.65				0.65	
M35-0.6		35	65	0.60	
M45-0.6		45	55	0.60	

The prepared mixes were then cast into 50×50×50 mm cubic molds, consolidated by a vibrating table and trowel finished. All samples were demolded after 24 hours and placed into respective curing environments for up to 28 days. The demolded RMC samples were subjected to accelerated carbonation (28 ± 2 °C, $80 \pm 5\%$ RH, 10% CO₂). Corresponding PC-based control samples were cured under water or in air (28 ± 2 °C, $80 \pm 5\%$ RH, ambient CO₂) to achieve maximum strength gain for comparison purposes.

(ii) Introduction of air-entrained agent (Chapter 4)

The SC of RMC and PC were measured according to BS EN 196-3-2016 as 0.63 and 0.30, respectively (BSI 2016). Two different water/binder (w/b) ratios were used in the preparation of RMC and PC pastes corresponding to $SC \pm 10\%$ of both binders (i.e. 0.56 and 0.69 for RMC; 0.27 and 0.33 for PC) to ensure similar workabilities. The AEA was included in certain mixes at an amount of 0.15% of the total cement component. The details of the mix compositions used in this study are listed in Table 3.7. The prepared mixes were then cast into 50×50×50 mm cubic molds, consolidated by a vibrating table and trowel finished. All samples were demolded after 24 hours. The demolded samples were subjected to two curing environments for up to 28 days: (i) natural (28 ± 2 °C, $80 \pm 5\%$ RH, ambient CO₂) and (ii) accelerated carbonation (28 ± 2 °C, $80 \pm 5\%$ RH, 10% CO₂) curing.

Table 3.7 RMC samples with different contents of water and air-entrained agent (AEA) under 10% CO₂ curing and PC samples under natural curing

Curing condition	Mix	Composition (wt.%)			w/b ratio
		RMC	PC	AEA	
Accelerated CO ₂	M0.56-A	100	0	0	0.56
	MA0.56-A			0.15	
	M0.69-A			0	0.69
	MA0.69-A			0.15	
	P0.27-A	0	100	0	0.27
	PA0.27-A			0.15	
	P0.33-A			0	0.33
	PA0.33-A			0.15	
Natural	M0.56-N	100	0	0	0.56
	MA0.56-N			0.15	
	P0.27-N	0	100	0	0.27
	PA0.27-N			0.15	

(iii) Introduction of PFA and GGBS (Chapters 4)

The concrete mixes prepared in this study were composed of 40% binder and

60% coarse aggregates. The binder components of each sample varied by containing only PC (P40), only RMC (M40), RMC with PFA replacement (M30-F10 and M20-F20) and RMC with GGBS replacement (M30-G10 and M20-G20). The water/binder (w/b) ratio of each mix was determined in accordance with the standard consistency (SC) of each binder (BSI 2016) to provide the same workability level for all samples. The mixing process started with the mixing of the dry materials first, followed by the addition of water and further mixing until a homogenous mix was obtained. The prepared mix was then cast into 50×50×50 mm cubic molds, consolidated by a vibrating table and trowel finished. All samples were demolded after 24 hours and placed into respective curing environments for up to 28 days. The demolded RMC and RMC-SCM samples were subjected to carbonation curing under 28±2 °C, 80±5% relative humidity (RH) and 10% CO₂. Corresponding PC samples prepared for comparison purposes were cured under sealed conditions (28±2 °C, 80±5% RH and ambient CO₂) to achieve maximum strength gain. All the sample compositions used in this study are listed in Table 3.8.

Table 3.8 RMC samples with different contents of PFA and GGBS replacements under 10% CO₂ curing and PC samples under natural curing

Sample name	Composition (wt.%)					w/b ratio	Curing condition
	RMC	PC	PFA	GGBS	Coarse aggregates		
M40	40	-	-	-	60	0.60	Accelerated CO ₂
M30-F10	30	-	10	-		0.52	
M20-F20	20	-	20	-		0.45	
M30-G10	30	-	-	10		0.53	
M20-G20	20	-	-	20		0.46	
P40	-	40	-	-		0.33	Natural

3.2.2 Introduction of calcined dolomite as a new RMC source

(i) Investigation of influence of calcined dolomite replacements on the mechanical performance and carbon sequestration of RMC formulations (Chapter 5)

The SC of RMC and D800 were measured according to BS EN 196-3 (BSI 2016) as 0.60 and 0.29, respectively. This led to the preparation of concrete samples containing 40% binder and 60% coarse aggregates. The water to binder (w/b) ratios ranged between 0.29 and 0.60, which were calculated according to Equation 3.1, where SC and C represent the standard consistency and content (i.e. weight fraction of total binder) of RMC and dolomite (D) binders, respectively.

$$SC_{Mix} = SC_{RMC} \times C_{RMC} + SC_D \times C_D \quad (3.1)$$

The binder component was composed of 100% RMC in the control sample M and 100% dolomite in D800, whereas different combinations of RMC and dolomite (D800) were used in samples M75D25 (75% RMC and 25% D800), M50D50 (50% RMC and 50% D800), and M25D75 (25% RMC and 75% D800). Concrete samples were prepared by mixing the dry components first, followed by the addition of water to the dry mix. All the mix compositions used in this study are listed in Table 3.9. The prepared mixes were then cast into 50×50×50 mm³ cubic molds, consolidated by a vibrating table and trowel finished. All samples were demolded after 24 hours and cured under accelerated carbonation (28±2 °C, 80±5% RH and 10% CO₂) for up to 28 days.

Table 3.9 RMC samples with different contents of calcined dolomite replacements under 10% CO₂ curing

Sample	Binder (wt.%)			Aggregates (%)	w/b	w/MgO	Curing condition
	RMC	D800	D900				
M	40	0	0	60	0.60	0.60	Accelerated CO ₂
M75D25	30	10	0	60	0.52	0.63	
M50D50	20	20	0	60	0.45	0.70	
M25D75	10	30	0	60	0.37	0.80	
D800	0	40	0	60	0.29	1.04	
D900	0	0	40	60	0.32	0.98	

(ii) Investigation of mechanical performance and carbon sequestration of RMC and calcined dolomite formulations under different curing conditions (Chapter 5)

The w/b of each composition was determined according to the SC 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 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 mix compositions used in this study are listed in Table 3.10.

Table 3.10 RMC samples and dolomite samples calcined at different temperatures (D700: 700 °C; D800: 800°C; D900: 900 °C) under 10% CO₂ curing

Sample	Binder (wt.%)		Aggregates (%)	w/b	Curing condition
	RMC	Calcined dolomite			
M	40	0	60	0.60	Accelerated CO ₂
D700	0	40	60	0.29	
D800	0	40	60	0.29	
D900	0	40	60	0.29	

3.2.3 Development of RMC-based strain-hardening composites with the ability to undergo self-healing (Chapter 6)

(i) Strain hardening behavior

The experimental program designed in this study consisted of two parts. The first part studied the effect of w/b and FA/b ratios on the rheology of fresh mixtures before the inclusion of fibers. The goal of this part was to determine a suitable mix design (i.e. w/b ratio and FA content) that led to a desired plastic viscosity and flowability for a good fiber dispersion. In the second part, during which PVA fibers were introduced into the mix design determined in the first part, the effects of the w/b ratio and curing age, whose increase can lead to a higher degree of carbonation and improve the strength development of RMC mixes (Unluer and Al-Tabbaa 2014), on the mechanical properties of RMC-SHC were studied.

The details of the seven different mix proportions prepared in the first part of the study are provided in Table 3.11. The notation for sample names followed a format of FA(X)-(Y), where X represented the FA content (i.e. as a percentage of the total binder) and Y represented the w/b ratio. A range of w/b (0.47-0.58) and FA/b (0-0.6) ratios were determined from preliminary samples prepared for each formulation. The sample preparation process

started with the dissolving of $\text{Na}(\text{PO}_3)_6$ in the pre-determined amount of water. This solution was then added to the dry mix of RMC and FA during the mixing process. A stopwatch was set to notify two minutes from the moment the solution was added to the dry RMC-FA mix.

Table 3.11 Mix proportions of fiber-free RMC mixtures prepared for rheology measurements.

*Sample	RMC (kg/m ³)	FA (kg/m ³)	Water (kg/m ³)	$\text{Na}(\text{PO}_3)_6$ (kg/m ³)	FA (%)	w/b	Solid (RMC+FA)) volume fraction
FA0-0.58	1102	0	639	64	0	0.58	0.35
FA30-0.47	840	360	570	57	30	0.47	0.42
FA30-0.53	789	338	595	59	30	0.53	0.39
FA30-0.58	744	319	617	62	30	0.58	0.37
FA60-0.47	462	693	548	55	60	0.47	0.44
FA60-0.53	435	653	573	57	60	0.53	0.42
FA60-0.58	411	616	596	60	60	0.58	0.39

* The rheology measurements performed on samples FA0-0.47 and FA0-0.53 were not presented as these fresh mixtures hardened too fast, resulting in incorrect results. Specifically, once the plate-to-plate spinning started, these samples immediately dislodged and were no longer in full contact with the upper plate.

As a certain level of plastic viscosity is crucial for good fiber dispersion and tensile ductility (Yang, Sahmaran et al. 2009), results from the first part of the study were used in the selection of w/b and FA/b ratios to be incorporated in the mix designs in the second part. Previous literature (Li and Li 2013) has shown that while the fiber dispersion coefficient increased with plastic viscosity, tensile ductility stabilized after a threshold fiber dispersion coefficient. This value corresponded to a plasticity of about 3.5 Pa·s, which was also adopted in this study for the preparation of samples used in the testing of tensile properties. Referring to the results obtained in the first part of the study to identify samples that demonstrated good fiber dispersion (e.g.

FA30-0.53), the three mix proportions listed in Table 3.12 were prepared to assess the tensile performance of RMC-SHC. For all the mix designs, the FA/b was fixed at 0.3, whereas the w/b ratio was kept at ≤ 0.53 according to the outcomes of the rheology measurements. A constant fiber fraction corresponding to 2% of the binder content was utilized in line with the previous literature on ECC (Li 2003).

Table 3.12 Mix proportions prepared for testing hardened tensile properties

Sample	RMC (kg/m ³)	FA (kg/m ³)	Water (kg/m ³)	Na(PO ₃) ₆ (kg/m ³)	PVA fiber (kg/m ³)	w/b	Curing duration (days)
RMC-0.53	799	342	601	59	26	0.53	7
RMC-0.47	853	365	573	53	26	0.47	7
RMC-0.41	864	370	510	51	26	0.41	7 and 28

To initiate sample preparation, RMC and FA were dry mixed in a planetary mixer for over 3 minutes, after which the prepared Na(PO₃)₆ solution was slowly added to form the fresh mixture. The mixing process continued for an additional 2-3 minutes until a uniformly mixed homogenous mixture was achieved, after which the PVA fibers were slowly added within 2 minutes. During the entire mixing process, the blade rotation speed was kept constant at 6.4 rad/s. The prepared mixture was cast into cubic (50x50x50 mm) and dogbone shaped molds, whose dimensions are shown in Fig. 3.6. The cast samples were stored in a sealed container, where silica gel was used for removing the excess moisture from the pastes to facilitate the penetration of CO₂ within the sample pore structure in the subsequent stage (Mo and Panesar 2012). After 3 days, samples were removed from their molds and cured in a carbonation chamber set at a CO₂ concentration of 10%, temperature of 30±1.5 °C and relative humidity (RH) of 85±5% (i.e. ambient levels in Singapore) for 7 days (Unluer and Al-Tabbaa 2013, Unluer and Al-Tabbaa 2015). The effect of curing duration was studied by exposing one of the prepared samples (RMC-0.41) to carbonation curing for a total of 28 days

under the same conditions.

Fig. 3.6 Illustration of uniaxial tensile test, showing dimensions of the dogbone specimen

(ii) Self-healing behavior (Chapter 6)

(a) Water and CO₂-based self-healing behavior

The same procedure mentioned in Section 3.2.3 (i) was followed in this study for sample preparation. The prepared mix designs are shown in Table 3.13. The dog-bone specimens were first pre-loaded at a loading rate of 0.02 mm/min under uniaxial tension to pre-determined tensile strain levels of 0% (control group), 0.5%, and 1%; after which, the specimens were removed from the loading machine and all the cracks were marked before the specimens were conditioned to engage autogenous healing. Four different environmental regimes were explored, including (i) direct exposure to laboratory air (A) for 20 days, (ii) alternative water and air conditioning (WA) for 20 days, i.e. 10 cycles of one day immersed in the water followed by one day in the laboratory air, (iii) alternative water and CO₂ conditioning (WC) for 20 days, i.e. 10 cycles of one day in the water and one day in a carbonation chamber, (iv) 10 days of CO₂ conditioning (C) where water was sprayed on specimen surface once a day. The temperature of air conditioning and water

conditioning was maintained at $22\pm 3^{\circ}\text{C}$; the relative humidity of the laboratory air was $75\pm 9\%$. The CO_2 conditioning was carried out in a carbonation chamber at a CO_2 concentration of 10%, temperature of 30°C , and RH of 90%. In total, 10 groups of specimens with three pre-straining levels and four conditioning regimes were studied for their performance of autogenous healing as summarized in Table 3.14.

Table 3.13 Mix proportions of RMC-based SHC for pre-strain test

RMC (kg/m^3)	FA (kg/m^3)	Water (kg/m^3)	$\text{Na}(\text{PO}_3)_6$ (kg/m^3)	PVA fiber (kg/m^3)	Fiber content (by volume)
864	370	510	51	26	2%

Table 3.14 Details of pre-straining levels and conditioning regimes

Group	No. of specimen	Conditioning regimes	No. of conditioning cycles	Preloading		
				Pre-strain level (%)	Number of cracks	Crack width (μm) [^]
A-0*	5	2 days in air	10	0	-	-
A-5	5			0.5	3.4 ± 2.2	47 ± 28
WA-0*	5	1 day in water / 1 day in air	10	0	-	-
WA-5	6			0.5	4.7 ± 2.3	36 ± 30
WA-10	5			1	8.6 ± 2.7	62 ± 15
WC-0*	5	1 day in water / 1 day in CO_2	10	0	-	-
WC-5	6			0.5	4.3 ± 2.5	33 ± 12
WC-10	5			1	7.4 ± 4.9	64 ± 50
C-0*	5	1-day in CO_2 [#]	10	0	-	-
C-5	6			0.5	5.6 ± 3.6	32 ± 26

* included as the control group cured under the same conditioning regime

water was sprayed on specimen surface once a day

[^] for individual specimen, the crack width=residual tensile displacement/crack number

(b) Bacteria-based self-healing behavior

The same procedure mentioned in Section 3.2.3 (i) was followed in this study

for sample preparation. The prepared mix designs are shown in Table 3.13. The main difference was that this study involved a new approach, bacterial healing, for the repair of cracks in RMC-fiber mixes. To prevent any damage to bacteria caused by mixing, instead of directly mixing the bacteria and urea into the prepared RMC-based mixes, the cracked samples were submerged into bacteria-urea (B-U) solution for 1 day, followed by air (A) curing for another 1 day. Another batch of samples was subjected to air/air (A/A) and water/air (W/A) conditions (i.e. 1 day under each condition), for comparison purposes. This regime was adopted to simulate the spray of bacteria-urea solution in real life, whereas the water/air condition simulated rainy/dry days in practice. The details of the healing regimes used in this study are presented in Table 3.15. Two concentrations of urea solution, corresponding to 1 and 2 M, were prepared by dissolving solid urea in distilled water. The temperature and RH used during all the conditions were kept at 22 ± 3 °C and $75\pm10\%$, respectively. At least 3 cracked dog-bone samples were used for each condition.

Table 3.15 Details of the healing regimes used in this study

Condition	Healing regime	Number of cycles	Total duration (days)
A/A	2 days in air	10	20
W/A	1 day in water / 1 day in air	10	20
B-1U/A	1 day in bacteria-1 M urea solution / 1 day in air	10	20
B-2U/A	1 day in bacteria-2 M urea solution / 1 day in air	10	20

3.3 Methodology

3.3.1 Foam index test

The foam index test, as explained in (Corr, Lebourgeois et al. 2002, Atahan, Carlos et al. 2008), was utilized to evaluate the air voids generated by air-

entrained agent (AEA) during mixing and investigate the compatibility between AEA and the binders used in this study through the following steps: (i) Preparation of a 100 ml solution containing an AEA concentration of 0.05%, (ii) mixing 20 ml of AEA solution with 4 grams of cement in a graduated cylinder, (iii) sealing and continuous shaking of the cylinder for 15 seconds and recording of the initial volume and (iv) recording of the final volume after 5 minutes. The absolute volume of the foam and the relative change between the initial and final volumes of RMC-AEA and PC-AEA mixes were used as indicators of foam stability.

3.3.2 Yield stress

The use of slump test for the evaluation of the workability/yield stress of fresh pastes with or without the inclusion of admixtures has been reported in several studies, where an admixture content of up to 1% of the cement content was used (Jiang, Kim et al. 1999, Ferraris, Obla et al. 2001, Şahmaran, Özkan et al. 2008). Yield stress (τ_0) of the pastes prepared in this study was calculated via the measurement of their flow diameter with a slump test through Equation 3.2, where “ W_x ” is the weight of the cement paste placed inside a truncated cone mould ($D_1 = 70$ mm, $D_2 = 100$ mm and $h = 50$ mm) and “ r ” is the radius of the spread paste (Melo, Aguilar et al. 2014). The initial weight of the prepared pastes was measured as soon as they were poured into the cone placed in the middle of a measuring platform. The cone was then lifted vertically upwards for 25 times during each measurement to allow the blend to flow on the platform. Once stable, two perpendicular diameters of the blend in its final form were measured. The test was repeated at least twice for each blend.

$$\tau_0 = W_x / (2\pi r^2) \quad (3.2)$$

3.3.3 Rheology

The fresh mixture was placed onto a 39 mm proliferated base plate on the

rheometer, equipped with a 39 mm P35 TiL top plate pressed against the mixture at 0.5 N. The rheology measurements were performed via a HAAKE MARS III 379-0400 rheometer, which was used to measure the shear resistance of the fresh mixtures at a designated rotation speed according to the test setup shown in Fig. 3.7.

Fig. 3.7 Measurement of sample rheology, showing (a) rheometer used and (b) test setup

3.3.4 Isothermal calorimetry

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 °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.

3.3.5 Optical microscopy

Nikon DS-Fi2 high resolution camera was used in the optical microscope analysis involving the use of NIS-Elements BR4.10 software.

3.3.6 Porosity

The porosities of samples before and after carbonation were calculated via Equation 3.3, 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 (i.e. calculated by measuring sample dimensions with a Vernier scale).

$$p = (m_{\text{sat}} - m_{\text{dry}}) / v * 100 \quad (3.3)$$

3.3.7 Density

The mass of each sample was recorded before and after accelerated carbonation and natural curing to calculate the change in mass due to carbonation. This was used to calculate the density of samples at different stages of carbonation, which was reported in triplicates.

3.3.8 Thermal conductivity

Thermal conductivity refers to the heat conduction property of a material and is defined as the temperature gradient divided by heat flow. It changes with the density and permeability of concrete (Howlader, Rashid et al. 2012). Thermal conductivity is highly related with the porosity of samples, and the porosity is also greatly determined by water/cement ratio and carbonation degree. Therefore, thermal conductivity is an indirect way to assess the porosity and carbonation degree of samples. Thermal conductivity measurements were investigated using a transient plane source, ThermTest Inc. Hot Disk® TPS 500 Thermal Constants Analyser. A 3.189 mm Kapton disk type sensor was used for the analysis. The sensor was sandwiched between two samples and the dimension of the sample is 50mm*50mm*50mm. The measurement time and the heating power were set to 20 seconds and 80 mW, respectively. All tests were conducted at a room temperature of 23 °C.

3.3.9 Water sorptivity

The prepared samples were tested for their water sorptivity before and after curing according to ASTM C1585-04 (ASTM 2013). To enable this, the cubic concrete samples were dried in oven set at 50 °C for 3 days, after which they were cooled under room temperature and covered with epoxy on the sides. The size of the concrete surface in contact with water, i.e. the inflow surface, was 50 x 50 mm. The mass of each sample was recorded at various times using an electronic balance. Water absorption (I) was calculated by dividing the variation in mass (Δm) with the concrete inflow surface area (a) and the density of water (ρ), as shown in Equation 3.4. The initial rate of water absorption (k , mm/seconds^{1/2}) was stipulated as the slope of the line that is the best fit to water absorption (I) plotted against the square root of time (t , seconds), as shown in, which is shown in Equation 3.5.

$$I = \Delta m / (a * \rho) \quad (3.4)$$

$$I = k * t^{0.5} \quad (3.5)$$

3.3.10 Resonance frequency (RF) measurement

The transverse resonance frequency (RF) of all samples was tested and recorded before and after healing periodically, which served as an indirect and simple approach for the evaluation of sample stiffness. RF was measured according to ASTM C215 (ASTM 2014), with a 200 mm span between the roller supports.

3.3.11 X-ray microtomography (μ -CT) analysis

μ -CT, performed with a SkyScan1183 scanner, a camera, and a FlatPanel sensor, was employed. The samples were fixed on a micro-positioning stage and scanned using a source voltage and current of 80 kV and 100 μ A, respectively. During the scan, the samples were rotated 360° in steps of 0.2°. A total of 1800 2D projections were obtained for each scan and a 3D

projection was built based on these 2D projections.

3.3.12 Compressive strength test

The compressive strength of the prepared concrete samples was measured by uni-axial loading in triplicates at various curing durations in accordance with the specifications of ASTM C109/C109M – 16 (ASTM 2013). The equipment used for this purpose was a Toni Technik Baustoffprüfsysteme machine, operated at a loading rate of 100 kN/min.

3.3.13 Uniaxial tensile strength test

The uniaxial tensile tests were conducted on at least three specimens for each mix design by using an Instron 5569. During this test, the loading rate was set at 0.02 mm/min and two LVDTs were used to determine the extension of the gauged length (60-70 mm).

3.3.14 pH value measurement

The pH measurement of the prepared samples was investigated in accordance with ASTM C25 (ASTM 2006). A Mettler Toledo pH meter was used for this purpose. During the measurement, 5 grams of sample powder was mixed into 100 grams of distilled water and stirred for 30 minutes and was let to stand for 30 minutes. Before the testing, the pH meter was calibrated.

3.3.15 X-ray diffraction (XRD), thermogravimetry/differential scanning calorimetry (TGA/DSC) and scanning electron microscope/energy-dispersive X-ray spectroscopy (SEM/EDX) analyses

Samples extracted from the cubes crushed during strength testing were stored in acetone to stop hydration, followed by vacuum drying in preparation for X-ray diffraction (XRD), thermogravimetric/differential thermal analysis (TGA/DSC) and scanning electron microscopy/energy-dispersive X-ray

spectroscopy (SEM/EDX) analyses.

The dried samples were ground down to pass through a 125 μm sieve before they were analysed under XRD and TG/DSC. XRD was recorded on a Philips PW 1800 spectrometer using Cu K α radiation (40 kV, 40 mA) with a scanning rate of 2° 2 θ /step from 5 to 80° 2 θ . Phase quantification was performed via the Rietveld refinement software TOPAS 5.0 with fundamental parameter approach (Cheary and Coelho 1992). TGA/DSC was conducted on a Perkin Elmer TGA 4000 equipment with a heating rate of 10 °C/min under nitrogen flow. The sample was first heated from room temperature to 40 °C and the temperature was kept for 10 min. Then, the temperature was increased from 40 at 10 °C/min up to the target calcination temperature at atmospheric pressure, which was kept for 0.5 h. And after which, the temperature further increased to 900 °C at 10 °C/min. The powder samples were dried in vacuum dryer for at least 3 days at room temperature during TGA/DSC. Prior to SEM analysis, the exposed section was coated with platinum under 30 mA current with a coating time of 30 seconds. The sample was then investigated via a field emission scanning electron microscope (FE-SEM, JOEL JSM-7600F) and energy-dispersive X-ray spectroscopy (EDX, Oxford X-max 80 mm²).

Chapter 4 INFLUENCE OF MIX DESIGN AND USE OF ADDITIVES ON THE PERFORMANCE OF RMC FORMULATIONS

This chapter presents the results obtained on the enhancement of carbon sequestration and the mechanical performance of RMC formulations through the analysis of the influence of (i) mix design (i.e. water, cement and aggregate contents) and (ii) use of additives (i.e. air-entrained agents (AEA)) and (iii) partial replacement of RMC with industrial by-products (i.e. pulverized fuel ash (PFA) and ground granulated blast furnace slag (GGBS)).

The first part assessed the influence of mix design on the hydration and carbonation of RMC-based concrete formulations by varying the water, cement and aggregate contents. The mix designs used in this part are shown in Table 3.6. Samples were subjected to accelerated carbonation under 10% CO₂ for up to 28 days and compared with corresponding PC-based samples. Their performance was analyzed by compressive strength, porosity, density, water sorptivity and thermal conductivity measurements. XRD, TGA/DSC and FESEM/EDX analyses were employed to investigate the formation of hydration and carbonation products and microstructural development.

The second part of the study investigated the influence of AEA on the performance and microstructure of RMC samples in comparison with PC samples under different water contents and curing conditions. The mix designs used in this part are listed in Table 3.7. Porosity, density, workability, strength, pH and thermal conductivity measurements were supported with XRD, TGA/DSC and SEM/EDX analyses.

The final part of this study investigated the performance of RMC-based formulations containing PFA and GGBS. The mix formulations of this part are shown in Table 3.8. Concrete samples, whose binder component was

composed of RMC with 0-50% PFA and GGBS replacement were subjected to carbonation curing for up to 28 days. The performance of each sample was analyzed and compared to corresponding PC-based samples via porosity, water sorptivity, compressive strength and thermal conductivity measurements. FESEM/EDX analysis was used to investigate the formation of hydrate and carbonate phases.

4.1 Influence of mix design (i.e. water, cement and aggregate contents) on the mechanical performance and carbon sequestration of RMC formulations

4.1.1 Results and discussion

4.1.1.1 Density and porosity

Fig. 4.1 shows the change in the densities of all samples cured for up to 28 days, which can provide a rough estimation of the extent of carbonation within the samples. Most of the samples demonstrated a constant increase in their density with curing age, which was associated with the progress of the hydration and carbonation reactions. These reactions enabled the reduction of the initial porosities and an associated increase in sample densities via the expansive nature of the hydrate and carbonate phases, whose formation led to the filling up of the initially available pore space. RMC samples revealed a higher increase in density over the PC samples (i.e. 4-7% vs. 0-2% at 28 days). This was associated with the formation of carbonate phases over the entire curing period. The highest increase in density was observed during the first 7 days of curing, which happened at a lower rate in subsequent curing durations, showing that the reactions slowed down after 7 days. The highest percentage increase in density reaching up to 7% over 28 days was revealed by the control sample M40-0.6, along with samples M40-0.55 and M45-0.6.

Fig. 4.1 Change in the density of RMC samples under 10% CO₂ curing and PC samples under air and water curing for up to 28 days

A reduction in the water content from a w/c ratio of 0.6 to 0.55 led to the highest increase in density at early ages (≤ 7 days). This was attributed to the faster diffusion of CO₂ through less saturated mediums. The opposite effect was observed when the w/c was increased to 0.65, leading to a slower diffusion of CO₂, which was reflected as a lower increase in density over the entire curing period. The higher contents of water in concrete samples can inhibit the diffusion of CO₂, thereby reducing the rate of the carbonation reaction and associated increase in density (Unluer and Al-Tabbaa 2013, Unluer and Al-Tabbaa 2014). Another factor to consider is the evaporation of water within the samples, which can increase with increased water contents (i.e. assuming all other parameters such as temperature, humidity and wind velocity are kept constant) (Almusallam, Maslehuddin et al. 1998, Topçu and Elgün 2004). This may have led to an increased evaporation degree in sample M40-0.65, which can cause a reduction in sample mass and density. Samples with different cement contents ranging from 35 to 45% revealed

similar densities during the entire course of carbonation. A slight increase in density was observed with an increase in the cement content of sample M45-0.6 and vice versa. This may be due to the carbonation potential of the cement powder, whose content within the overall concrete mix design not only influences the initial density due to its fine nature, but also the diffusion rate of CO_2 and the overall degree of carbonation. Although aggregates occupy a majority of the sample volume, their role in the carbonation process is secondary as their imperfect packing arrangement merely provides the necessary porosity for the diffusion of CO_2 within the sample pore system. The formation of hydrate and carbonate phases is mainly dependent on the properties of the cement paste and pore structure, where the reaction between brucite and CO_2 takes place as shown in Equations 2.9-2.13. An optimum cement content that does not block the continuous ingress of CO_2 by filling up the available pore network can facilitate the carbonation reaction via increased amount of reactants. This can explain the higher increase in the density of sample M45-0.6 as opposed to samples with lower cement contents.

The porosities of all samples cured for up to 28 days are shown in Fig. 4.2. In line with the increase in densities, a reduction in the porosities of all RMC samples was observed as carbonation progressed. Initial porosities of RMC samples before carbonation ranged between 23-31%, whereas PC samples revealed a porosity of 10% before carbonation. Similar to the density results, the porosities of PC samples did not indicate a major change over the 28 days of curing, while RMC samples achieved porosities of as low as 7-11% due to the formation of carbonate phases. Unlike RMC samples, the lack of a major change in the porosities of PC samples was due to the different curing mechanisms samples containing these two binders were exposed to (i.e. hydration vs. carbonation). As evident from the overall density and porosity data, PC samples revealed almost constant porosities along the entire curing process as their strength gain mechanism was due to the hydration process, resulting in a small reduction in porosity.

Fig. 4.2 Porosity of RMC samples under 10% CO₂ curing and PC samples under air and water curing for up to 28 days

Alternatively, RMC samples demonstrated an up to 21% decrease in their porosities at 28 days. It was mainly the expansive formation of HMCs that resulted in this significant reduction in the initial porosities of RMC samples (Unluer and Al-Tabbaa 2013, Unluer and Al-Tabbaa 2014), which revealed very similar or even lower porosity results than PC samples at the end of the 28-day curing period. In line with the density results, a majority of the porosity reduction took place during the first 7 days of curing as the carbonation reaction slowed down afterwards. This was attributed to the slower diffusion of CO₂ after the formation of a dense carbonate network within the initially available pore space. The initially formed HMCs can form a dense layer around the MgO and brucite crystals, hindering further access of CO₂ to the uncarbonated hydrate phases (Harada, Simeon et al. 2015). This results in the reduction of the rate of porosity change, which stabilizes once the carbonation reaction ceases.

RMC samples with reduced water contents (M40-0.55) revealed lower initial porosities as expected, since the water content controlled the capillary porosity of concrete samples. An increase in the w/c ratio from 0.55 to 0.6 led to an increase in the initial porosity from 23 to 31%. The initial water content of samples also influenced the change in their porosities, which was an indication of the extent of carbonation. Sample M40-0.6 revealed a higher change in porosity than M40-0.55 and M40-0.65, potentially because of a higher degree of brucite and HMC formation due to CO₂ absorption. When compared to the water content, the effect of cement content on porosity was less pronounced. Sample M35-0.6 indicated a lower porosity than the corresponding samples with higher cement contents, M40-0.6 and M45-0.6, which possessed similar porosities at all curing durations. The slightly lower porosity of M35-0.6 could be attributed to the higher aggregate content of this particular sample, which may have absorbed some of the unbound water to achieve saturation. This may have resulted in the reduction of the effective water content and thereby the initial porosity of this particular sample (Erntroy and Shacklock 1954, Singh 1958).

4.1.1.2 Water sorptivity

Measurements of water sorptivity were performed to assess the capillary suction of unsaturated concrete samples with different compositions when placed in contact with water (Neville 1995). The results obtained by this measurement could be an indication of the carbonation ability of each sample as water ingress could reflect the pore structure and provide an indirect approach of the measurement of interconnected capillary pores (Basheer, Kropp et al. 2001). The main output of this test was the initial rate of water absorption of samples before and after 7 days of curing (i.e. the slope of the second rate of water absorption was almost zero), as reported in Fig. 4.3.

Fig. 4.3 Water sorptivity of RMC samples before and after 7 days of CO₂ curing and PC samples before and after 7 days of water curing

All samples experienced a significant reduction in their water sorptivity values after hydration and carbonation due to the densification of their microstructures. This was enabled via the formation of hydrate and carbonate phases during the measured time frame (Mo and Panesar 2012). PC samples indicated a much lower water sorptivity than corresponding RMC samples before the curing process. This difference between the sorptivity values of RMC and PC samples greatly diminished after curing. The progress of hydration within the PC samples led to a reduction in the capillary pore space over time, thereby reducing their water sorptivity (El-Dieb 2007).

Out of all the RMC samples, sample M40-0.55 demonstrated the lowest water sorptivity values before carbonation (i.e. up to 60% lower than corresponding samples with higher water contents), owing to its relatively lower initial capillary porosity. These results were in agreement with the porosity values presented in Fig. 4.2, outlining PC samples for their much lower porosities than RMC samples and M40-0.55 for its lower porosity than all other RMC samples. The introduction of carbonation to sample M40-0.55 reduced its

water sorptivity to a value slightly higher than the corresponding measurement of M40-0.6. This could be an indication of the slightly lower hydration/carbonation of sample M40-0.55 when compared to M40-0.6.

When samples with different cement contents were compared, sample M35-0.6 revealed a lower water sorptivity than the corresponding samples M40-0.6 and M45-0.6, which was in line with the porosity results. This could be attributed to the smaller paste and thereby the lower capillary pore content within this sample when compared to samples with higher cement contents. A similar finding was reported by previous studies (Kolias and Georgiou 2005), who highlighted the link between capillary absorption and volume of cement paste, as well as the water content. A higher capillary absorption is expected in samples with higher water contents and paste volumes, when all the other parameters are kept constant. Overall, the results were in agreement with previous findings that revealed the strong relationship between carbonation depth and water sorptivity (Bai, Wild et al. 2002), which depends on the w/c ratio as well as the cement and aggregate contents of concrete mixes.

4.1.1.3 Compressive strength

The compressive strength of all RMC and PC samples cured for up to 28 days is shown in Fig. 4.4. PC samples cured in air and water achieved 28-day strengths of up to 55 and 68 MPa, respectively. The higher strengths demonstrated by PC samples cured under water was as expected since the lack of water in air curing may have led to a limited hydration and potential shrinkage accompanied with surface cracking (Mindess, Young et al. 1981). Subjecting RMC sample M40-0.55 to accelerated carbonation led to similar 28-day strengths of up to 62 MPa. This is a clear indication that RMC samples are able to achieve similar strengths to PC samples when the right mix design and curing conditions are provided. In PC samples, the hydration process and the formation of major hydrate phases such as C-S-H leads to strength gain (Rostami, Shao et al. 2012), whereas RMC formulations rely on the progress

of carbonation and the associated development of a dense carbonate network (Unluer and Al-Tabbaa 2013).

Fig. 4.4 Compressive strength of RMC samples under 10% CO₂ curing showing (a) samples with different water contents, (b) samples with different cement contents and (c) all samples and PC samples under water and air curing for up to 28 days

The effect of water content on the strength development of RMC samples can be observed via a comparison of samples M40-0.55 and M40-0.65 with the control sample M40-0.6, as shown in Fig. 4.4(a). Reducing the w/c ratio from 0.6 to 0.55 led to a constant increase in the strength of RMC samples at all curing durations. A similar trend was observed when the w/c ratio was increased from 0.6 to 0.65, leading to a reduction in strength at all durations. Accordingly, 28-day strength values of 62, 45 and 32 MPa were achieved by samples M40-0.55, M40-0.6 and M40-0.65, respectively. This particular trend observed in strength development can be explained by the reduction in the porosity of samples over time due to the continuous progress of carbonation (Unluer and Al-Tabbaa 2014). Another factor influencing the rate and degree of carbonation is the diffusion rate of CO₂ within the samples, which can be determined by the water content and the saturation rate of pores. Mixes with higher water contents (w/c of 0.65) can demonstrate a slower diffusion of CO₂ due to the saturated pore network, thereby leading to lower strength gain. Decreasing the water content (w/c of 0.55) not only led to samples with a lower initial porosity but may have also increased the diffusion of CO₂ within the samples, thereby leading to higher strength gains.

The effect of cement content on the strength development of RMC samples can be observed via a comparison of samples M35-0.6 and M45-0.6 with the control sample M40-0.6, as shown in Fig. 4.4(b). An increase in the RMC content from 35% to 45% generally resulted in an increase in the compressive strength of all samples, albeit less significantly than the water content. Strengths as high as 52 MPa were achieved by the M45-0.6 sample after 28 days, which was 16% higher than the corresponding strength of the control sample (45 MPa). Alternatively, a similar reduction in the water content led to a 38% increase in the strength of the control sample by revealing a 28-day strength of 62 MPa, as reported earlier. This is mainly because the main issue in RMC formulations is the optimization of the use of RMC by enabling the complete carbonation of the cement component. Although a higher cement content can intrinsically lead to slightly higher strengths via the generation of

a denser structure, the critical issue of fully utilizing the included cement component by facilitating its participation in the carbonation reaction still remains. Therefore, changing the cement content has a smaller influence on the overall mechanical performance of the designed formulations than other parameters within the mix design that can enable the continuous ingress of CO₂ through the available pore network. This was also further confirmed with a two-way analysis of variance (ANOVA) conducted on the 28-day strength data of the different samples. The significance of each parameter (water and cement content) was investigated via the calculation of the F-ratio. The bigger F-ratio revealed by samples with different water contents as opposed to that of samples with different cement contents (i.e. 3 vs. 1.2) highlighted the larger significance the initial water content had on the strength development of RMC-based concrete formulations.

4.1.1.4 Crystal mineral components

The major phases within RMC samples after 14 days of 10% CO₂ curing via XRD patterns are shown in Fig. 4.5. Amongst some minor peaks of other phases, the main carbonate phase observed was hydromagnesite as well as a minor formation of dypingite. Many of the strong and weaker peaks of hydromagnesite (PDF #025-0513) could be seen in the XRD patterns presented, confirming its presence. Hydromagnesite has some of its highest intensity peaks at 15.3°, 30.8° and 13.7° 2θ, which are similar to those of dypingite and hence are expected to overlap on the XRD spectra. In addition to HMCs, all selected samples exhibited the presence of unhydrated MgO and uncarbonated brucite. Table 4.1 lists the quantities of major phases within the pastes extracted from cured samples. All samples indicated hydromagnesite contents ranging between 8-14% of the overall mix composition, whereas the rest was composed of residual MgO (38-55%) and brucite (37-52%). The relatively high contents of the unhydrated MgO were an indication of the low utilization rate of RMC in the hydration and subsequent carbonation reactions. These results clearly imply the potentially higher strengths RMC formulations can achieve if their complete carbonation

is realized.

Fig. 4.5 Major phases within RMC samples after 14 days of 10% CO₂ curing via XRD patterns (B: Brucite, H: Hydromagnesite, D: Dypingite, P: Periclase)

Table 4.1 Quantification of major phases within samples under 10% CO₂ curing for 14 days

Mix	MgO (wt.%)	Brucite (wt.%)	Hydromagnesite (wt.%)
M40-0.55	54.8	37.4	7.9
M40-0.6	46.9	41.9	11.3
M40-0.65	38.0	52.0	10.0
M35-0.6	43.5	42.6	13.9
M45-0.6	41.8	44.9	13.3

The effect of initial water content was reflected in the degree of hydration expressed in terms of the brucite content. An increase in the water content led to a higher amount of brucite accompanied with a lower residual MgO content, as expected. Alternatively, the hydromagnesite content did not reveal a clear trend with respect to the initial water content. The control sample, M40-0.6, indicated a higher hydromagnesite content than M40-0.55 (11% vs. 8%) although the former had achieved a lower strength (45 vs. 62 MPa). This highlights that strength development is not only dependent on the amount of carbonate phases, but also on the morphology of these carbonates (De Silva, Bucea et al. 2009). Considering its lower hydromagnesite content, another factor that may have played a role in the strength development of M40-0.55 was its dense structure achieved via the use of a lower water content than the other mixes. This was also evident from the density and porosity results presented earlier. This outcome was in line with the water sorptivity results, showing that M40-0.55 revealed a slightly higher water sorptivity than M40-0.6 after carbonation, corresponding to a lower amount of carbonate phases albeit its higher strengths.

Water plays a key role in the continuation of the hydration process, which leads to the formation of brucite that reacts with CO_2 to form carbonate phases. As sample M40-0.55 had a lower water content than other samples, it demonstrated a lower hydration degree (i.e. highest residual MgO content of 55%) due to its limited hydration. This was also reflected as a lower hydromagnesite content as the carbonation reaction is dependent on the extent of the preceding hydration process and the formation of brucite. An opposite effect was seen in samples with higher water contents, which experienced a higher conversion rate of MgO into brucite. However, it must be noted that excessive water present within the pore structure can also prohibit the diffusion of CO_2 , leading to a reduction in the extent of carbonation. This can explain the lower hydromagnesite content of sample M40-0.65 than M40-0.6 (10 vs. 11%) in spite of its initially higher brucite content (52 vs. 42%).

In line with the strength results, the phase quantification of samples M35-0.6 and M45-0.6 with different cement contents did not indicate major differences and revealed similar brucite and HMC contents of 43-45% and 13-14%, respectively. These were consistent with the previous findings, showing that changing the cement content did not have a major influence on the contents of the final phases and sample performance as a majority of the initially used RMC remained unutilized.

4.1.1.5 Carbon sequestration

The weight loss of RMC samples after 14 days of 10% CO₂ curing from 40-900 °C via TGA and DSC curves is presented in Fig. 4.6. Three major decomposition steps in accordance with the previous literature (Frost, Bahfenne et al. 2008, Vágvölgyi, Frost et al. 2008, Ballirano, De Vito et al. 2010, Hollingbery and Hull 2010, Frost and Palmer 2011, Jauffret, Morrison et al. 2015, Purwajanti, Zhou et al. 2015) were identified as:

(i) 50 to 320 °C: Dehydration of water bonded to HMCs ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O} \rightarrow 4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 + 4\text{H}_2\text{O}$ (Vágvölgyi, Frost et al. 2008, Ballirano, De Vito et al. 2010, Frost and Palmer 2011, Jauffret, Morrison et al. 2015, Purwajanti, Zhou et al. 2015)).

(ii) 320 to 480 °C: Dehydroxylation of HMCs ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \rightarrow 4\text{MgCO}_3 + \text{MgO} + \text{H}_2\text{O}$) and decomposition of uncarbonated brucite ($\text{Mg}(\text{OH})_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$) (Ballirano, De Vito et al. 2010, Hollingbery and Hull 2010, Frost and Palmer 2011, Jauffret, Morrison et al. 2015).

(iii) 480 to 900 °C: Decarbonation of HMCs ($\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$) (Frost and Palmer 2011, Jauffret, Morrison et al. 2015).

Fig. 4.6 Weight loss of RMC samples after 14 days of CO₂ curing from 40-900 °C via TGA and DSC curves

Table 4.2 lists a summary of weight losses associated with each reaction taking place at the temperature ranges listed above, along with the corresponding H₂O and CO₂ contents of all RMC samples. The loss of H₂O associated with brucite decomposition was differentiated from the dehydroxylation process of HMCs that took within the same temperature range via the data presented earlier in Table 4.1. The total weight loss increased with the water content, which was associated with a higher brucite content. In line with the XRD quantification results, sample M40-0.6 revealed a higher CO₂ loss corresponding to a higher HMC content than corresponding samples with different water contents (M40-0.55 and M40-0.65). This was

consistent with earlier explanations highlighting the importance of the morphology of the carbonate phases, rather than their content, in strength development. Alternatively, variations in the cement content did not influence the total CO₂ content of different samples, which was almost the same at around 15% for all three samples. The similar total weight losses (39%) revealed by these samples were in line with the strength results, indicating a direct relationship between the extent of hydration and carbonation reactions and mechanical performance.

Table 4.2 A summary of weight loss of samples obtained by TGA after 14 days of 10% CO₂ curing

Mix	Weight loss (wt.%)					Total
	50- 320 °C	320- 480 °C	480- 900 °C	H ₂ O (brucite)	CO ₂ (HMCs)	
M40-0.55	7.8	23.4	3.1	11.6	14.9	34.3
M40-0.6	10.7	25.3	3.2	13.0	15.4	39.1
M40-0.65	10.5	26.2	3.0	16.1	13.1	39.8
M35-0.6	10.6	25.2	3.3	13.2	15.3	39.1
M45-0.6	10.1	25.7	3.2	13.9	14.9	39.0

4.1.1.6 Microstructures

Fig. 4.7 shows the microstructural images of the two best performing RMC-based samples M40-0.55 and M40-0.6 after 14 days of 10% CO₂ curing via scanning electron microscope. The main carbonate phase observed in both samples was hydromagnesite, which is defined by its rosette-like structure. As also reported earlier by the XRD and TGA results, hydromagnesite was accompanied with brucite and periclase crystals. When compared to M40-0.6, M40-0.55 revealed a denser and more closely packed formation of hydromagnesite, which could explain its higher strength results. These

microstructures were supported with an elemental composition analysis of the same samples shown in Fig. 4.7. The details of the composition of each sample are listed in Table 4.3. Similar to the XRD and TGA quantification results, sample M40-0.6 revealed a higher carbon content than the corresponding sample M40-0.55, in spite of its lower strength.

Fig. 4.7 Microstructural images of samples under CO₂ curing for 14 days
(a)-(b) M40-0.55 and (c)-(d) M40-0.6 via scanning electron microscope

Table 4.3 Elemental composition analysis of selected samples after 14 days
of 10% CO₂ curing

Mix	C (%)	O (%)	Mg (%)	Impurities (%)
M40-0.55	12.3	50.1	34.1	3.5
M40-0.6	14.6	40.3	30.6	14.5

This can be explained via a consideration of all factors that influence the microstructural evolution and thereby the performance of RMC formulations. One of the main factors that contribute to the network structure is the binding strength and morphology of carbonates (De Silva, Bucea et al. 2006, Mo and Panesar 2012). The inter-connected and well-developed HMC crystals give rise to the formation of a strong network, leading to improved strength. Another important factor is the reduction in the initial porosity and associated microstructure densification caused by the expansive formation of carbonate phases via the reaction between brucite and CO₂. This was confirmed by the rapid reduction in porosity, increase in density and strength development of RMC samples during the first seven days of carbonation.

When all the aforementioned factors are considered, it is evident from the presented results that the initial water content within the samples had a significant influence on the overall porosity. A reduction in the water content enabled lower porosities. This had a direct influence on the final strength of samples and was evidently more crucial than the total carbonation degrees achieved by each sample.

4.1.1.7 Thermal conductivity

Mix design, including the cement, aggregate and water content, as well as the curing conditions have a direct influence on the thermal conductivity of concrete (Morabito 1989, Neville 1995). Table 4.4 lists the thermal conductivity values of all samples after 7 days of 10% CO₂ curing. The thermal conductivities of RMC samples were higher than corresponding PC samples due to the different cementitious components in each system. Amongst RMC samples, the thermal conductivity noticeably increased with increasing water content. This was associated with the larger porosity of samples with higher water contents, leading to higher conductivities (Wong, Glasser et al. 2007, Collet and Prétot 2014). Samples M35-0.6 and M40-0.6 revealed similar conductivity values, whereas a further increase in the cement content in sample M45-0.6 led to a decrease in thermal conductivity. This

could be because of the lower aggregate content of sample M45-0.6 when compared to M35-0.6 and M40-0.6. The cement binder generally possesses a lower thermal conductivity than aggregates. A reduction in the aggregate content may have led to a decrease in the thermal conductivity of M45-0.6 (Kim, Jeon et al. 2003).

Table 4.4 Thermal conductivity of samples after 7 days of 10% CO₂ curing

	M40-0.55	M40-0.6	M40-0.65	M35-0.6	M45-0.6	PC-air	PC-water
Thermal conductivity (w/mk)	1.79	2.01	2.17	1.97	1.87	1.40	1.26

4.1.2 Conclusion

1. The two main parameters investigated in this study (i.e. water and cement contents) not only influenced the initial density, porosity and thereby the final performance of the designed formulations, but also other parameters such as their thermal conductivity. The initial water content was determined as the main parameter controlling the final properties of RMC samples, which demonstrated a substantial increase in their density and an associated decrease in porosity over 28 days of curing due to the expansive formation of carbonate phases. A majority of this change took place during the first 7 days, showing that the carbonation process relatively slowed down afterwards. Alternatively, PC samples revealed negligible changes in their density and porosities due to the different strength gain mechanisms the two binder systems relied upon.

2. The compressive strength of RMC samples increased with a reduction in the w/c ratio. This was associated with lower porosities of the drier samples, along with the faster diffusion of CO₂ within dry mediums. Sample M40-0.55 (i.e. containing 40% cement and 60% coarse aggregates at a w/c ratio of 0.55) revealed the highest increase in density and the lowest porosity after

carbonation and achieved the highest strength out of all the RMC samples, reaching 62 MPa at 28 days. When compared to samples with lower strength results, the lower amount of phase formations obtained in this sample highlighted the importance of the initial mix design that directly influenced the porosity and controlled the overall strength development. Strengths of RMC samples were comparable with those of PC samples cured in air (55 MPa) and water (68 MPa), showing that RMC-based concrete can compete with PC-based concrete in terms of mechanical performance, even without an extensive optimization of its strength gain process.

3. Another factor that contributed to the mechanical performance of RMC samples was the morphology of the formed carbonates, rather than their quantity. The densification of the sample microstructures, enabled via the formation of hydrate and carbonate phases that filled in the initially available pore space, was an indication of the extent of the carbonation reaction. The water content as well as the paste volume had a direct influence on these properties by determining the overall pore volume, showing that the carbonation degree can be further increased with the optimization of these parameters. The mechanical performance and associated microstructural development of RMC samples can be further improved with an extensive optimization study focusing on other mix design parameters along with the curing conditions.

4.2 Influence of use of additives (i.e. air-entrained agents (AEA)) on the mechanical performance and carbon sequestration of RMC formulations

4.2.1 Results and discussion

4.2.1.1 Foam index test

The foam index test revealed the compatibility of AEA with RMC or PC by indicating the change in the foam volume within a given time frame. The foam

volume of AEA, AEA+RMC and AEA+PC samples are presented in Fig. 4.8 in terms of the free volume of the graduated cylinder used during this test. All samples experienced an obvious decrease in their foam volume after 5 minutes. The foam generated with the suspended solids indicated that there is either physical adsorption of the surfactant by the cement particles or a restraining effect of polyvalent cations (Mg^{2+} and Ca^{2+}) or anions (OH^-) released by RMC or PC. The use of AEA with RMC revealed a more stable output than its use with PC. The AEA+PC sample indicated a considerable reduction in foam volume even after a few seconds of initial shaking, which continued over time. In PC-based mixes, Ca^{2+} present in the solution could have prevented foaming. Alternatively, the lower solubility of RMC resulted in the release of a lower amount of Mg^{2+} than Ca^{2+} , thereby maintaining a higher volume than PC-based samples. The higher concentration of OH^- in PC-based samples (i.e. due to the higher solubility of $Ca(OH)_2$ than $Mg(OH)_2$) may have also exerted a restraint on the foaming process, thereby explaining the higher stability of foam within the RMC-based samples.

Fig. 4.8 Free volume of AEA, AEA+RMC and AEA+PC mixes

4.2.1.2 Yield stress

The rheological properties (e.g. yield stress and viscosity) of the prepared pastes have a direct influence on their overall void structure and stability (Du and Folliard 2005). Table 4.5 presents the yield stress values of RMC samples and the corresponding standard deviation of each measurement. The introduction of AEA reduced the yield stress of the M0.56 sample by ~50%, which can be attributed to the large number of small, spherical and well-dispersed air voids that formed in the paste due to the presence of the AEA. These voids acted as air cushions between the particles, which reduced the friction and interlocking effect, thereby improving the overall workability. The yield stress of the sample containing extra water, M0.69, remained relatively stable after the introduction of AEA. This is related to the higher water content of this sample, which resulted in a smaller yield stress and lower viscosity than the M0.56 sample even without the introduction of AEA. The reason behind the lack of change in the yield stress of this sample with the introduction of AEA can be attributed to the instability of air bubbles at high w/b ratios (Neville 1995). This is because the mobility of air bubbles depends on their size and the viscosity of the paste and can be limited if their buoyancy forces are not sufficient to break the yield stress exerted by the bulk cement paste. Mixes with higher viscosities can apply a barrier that reduces the coalition of adjacent air bubbles, thereby leading to the formation of stable small air bubbles (Du and Folliard 2005).

Table 4.5 Yield stress of selected RMC fresh paste

Sample / Yield stress	M0.56	MA0.56	M0.69	MA0.69
τ_0 (Pa)	479.7	250.4	90.3	94.2
Standard deviation (Pa)	18.1	8.8	5.3	1.9

4.2.1.3 Porosity

The diffusion of CO₂ within the cement matrix depends on the overall porosity as well as the interconnectivity of the pore network, which is governed by the permeability of the pore structure (Garboczi and Bentz 1996, Ferraris, Obla et al. 2001). A higher content of interconnected pores can translate into a higher degree of carbonation and thereby strength gain in RMC samples, whose porosities, along with those of PC samples, are listed in Table 4.6. PC-based samples indicated the lowest porosity values amongst all samples, independent of the AEA content. RMC-based samples M0.56 and M0.69 without AEA revealed similar porosities (~40% vs. 44%). A slight increase in the porosity was observed in samples with higher water contents as expected, due to their larger proportion of capillary pores. The porosity of M0.69 (i.e. sample with the higher water content) remained stable with the introduction of AEA, which was consistent with the yield stress measurements presented earlier in Table 4.5. However, the introduction of AEA to M0.56 (i.e. sample with the lower water content) resulted in a decrease in porosity from 40% to 35%. A reduction in porosity was also observed in the PC-based P0.27 sample, whose porosity decreased from 31% to 29% with the introduction of AEA. A similar finding was reported in other studies (Pigeon and Pleau 2010), which showed that the introduction of AEA can reduce the porosity of mixes containing low water contents. The air voids produced by AEA can also reduce the water absorption capacity of the capillary pore system via the generation of a lower capillary suction (i.e. sorptivity), thereby influencing the porosity measurements that are dependent on water absorption (Wong, Pappas et al. 2011).

Table 4.6 Porosity of selected RMC and PC samples before carbonation

Sample / Porosity	M0.56	MA0.56	M0.69	MA0.69	P0.27	PA0.27
Porosity (%)	40.2	35.1	43.9	43.5	31.2	28.7
Standard deviation (%)	0.7	0.7	0.1	0.4	0.2	0.1

4.2.1.4 Density

The change in the densities of selected RMC and PC samples subjected to accelerated and natural curing conditions is shown Fig. 4.9. An increase in the density of samples subjected to accelerated carbonation was observed in line with the carbonation reaction. This was more pronounced for RMC samples, which indicated a 12.5% increase in density over 28 days of curing. The higher density gain of RMC samples was enabled by their initially higher porosities, which facilitated the diffusion of CO₂ within the pore solution under accelerated carbonation conditions. The carbonation process led to the expansive production of carbonate phases, which increased the overall density. Although the introduction of AEA into RMC samples did not influence the change in density in the shorter term (≤ 7 days), it led to higher densities in the longer term by increasing the available pore space for CO₂ ingress. The use of AEA within RMC samples revealed up to a 14.8% increase in the densities of samples cured for 28 days, which was 2.3% higher than those of the corresponding RMC samples without AEA.

Fig. 4.9 Change in the density of selected RMC and PC samples subjected to accelerated carbonation and natural curing conditions

PC samples without AEA led to stable densities over time, which only increased by 1.5-2% over the entire curing period albeit the accelerated carbonation conditions they were subjected to. The lower increases in the density of PC samples could be attributed to their lower water contents when compared to corresponding RMC samples (i.e. w/b of 0.27 vs. 0.56), leading to lower initial porosities. These initially lower porosities may have limited the extent of carbonation of PC samples as porosity is one of the controlling parameters of CO₂ diffusivity (Houst and Wittmann 1994), thereby resulting in smaller increases in density. The use of AEA with PC had a more profound effect than it did with RMC as it led to an increase in the density of samples at all curing durations, resulting in an overall density increase of 5.3% at 28 days.

A different scenario was observed when RMC and PC samples were subjected to natural curing. RMC samples indicated a reduction in their density over time, which was more obvious with the introduction of AEA. This was attributed to the loss of available water over time under ambient curing conditions. As MgO has a low solubility in ambient conditions, the hydration process takes place slowly and to a smaller extent than those of PC samples. When not utilized in the hydration reaction, the free water can be lost through the pore network over time, thereby resulting in a reduction of the sample density with time. Since the increase in the density of RMC based samples is based on the progress of the carbonation reaction and the formation of HMCs, the lower CO₂ concentration (0.04%) was not sufficient for any noticeable carbonation within the given time period. Alternatively, PC-based samples that relied on the hydration process for strength gain maintained their densities in natural curing independent of the inclusion of AEA and revealed almost no change over the 28-day curing period. These results highlighted the importance of porosity under different curing conditions. While higher porosities, enabled by the higher initial water contents or the use of AEA, were preferred for the continuation of the carbonation reaction under elevated CO₂ concentrations, a different scenario was observed when the same samples

were subjected to natural curing.

4.2.1.5 Compressive strength

The compressive strengths of RMC and PC samples subjected to accelerated and natural curing conditions are shown in Fig. 4.10(a) and (b), respectively. While PC samples without the inclusion of AEA (P0.27 and P0.33) revealed the highest 28-day strengths of 65 MPa under accelerated carbonation, RMC samples achieved strengths of 36 MPa at 28 days, as seen in Fig. 4.10(a). In line with the porosity results presented in Table 4.6, the differences in the strengths of PC and RMC samples could be attributed to the lower porosity of the former, provided by the lower w/b ratios within the initial mix design. The influence of carbonation on strength development was much more obvious for RMC samples, whose strengths increased from 4 to 36 MPa from 1 to 28 days of carbonation. This was because RMC-based formulations rely on the formation of carbonate phases for strength gain, whereas the extent of the hydration process determines the strength development in PC samples.

Fig. 4.10 Compressive strength of RMC and PC samples subjected to (a) accelerated carbonation and (b) natural curing

The effect of water content on strength was more pronounced for RMC samples subjected to accelerated carbonation. M0.56 samples (w/b of 0.56)

led to higher strengths than corresponding M0.69 samples (w/b of 0.69) at all curing durations. This could be attributed to the lower initial capillary porosity and the faster diffusion of CO_2 within samples containing lower water contents, which could enable a more extensive carbonation than samples whose pores were relatively more saturated. The higher carbonation degrees of M0.56 samples may have led to a higher amount of HMC production, which can fill up the available pore space and thereby reduce the overall porosity and increase strength. This was also confirmed earlier by the porosity values presented in Table 4.6, which indicated that M0.56 had a lower porosity than M0.69 before curing commenced. The role of carbonation in reducing the overall sample porosity was also supported by the changes in the density of M0.56 samples, which demonstrated a 12.5-14.8% increase in their density over 28 days of accelerated carbonation, as shown in Fig. 4.9.

For PC-based samples, the use of AEA was more influential on strength development than the initial water content. While the use of different w/b ratios did not drastically change the strength results, the inclusion of AEA led to ~60% reduction in the strength of PC samples over 28 days of curing. This was mainly because the strength development of PC samples is based on the reduction of the initial porosity via the continuation of the hydration reaction, at the end of which C-S-H and Ca(OH)_2 formation is expected (Rostami, Shao et al. 2012). This was confirmed by the natural curing results shown in Fig. 4.10(b), which highlighted that PC based samples achieved similar strengths regardless of the carbonation conditions (i.e. accelerated or natural). The introduction of AEA may have increased the susceptibility of the PC samples to carbonation, which could result in the conversion of hydrate phases into CaCO_3 and SiO_2 , thereby reducing the overall strength. The presence of AEA may have also increased the overall void volume within the paste structure, which could have an adverse effect on sample performance.

Alternatively, the use of AEA in RMC samples led to similar 28-day strength results as those that did not incorporate any AEA, albeit their slower strength

gain at early ages. The lower initial strength results of MA0.56 with respect to M0.56 could be attributed to the higher air void content introduced via the use of AEA (Van den Heede, Furniere et al. 2013), whereas this was compensated with the increased CO₂ diffusion and overall degree of carbonation over longer curing periods (Wong, Pappas et al. 2011). M0.56 achieved over 90% of its overall strength gain in 7 days, after which strength gain was stabilized. This could be due to the formation of a carbonate layer around the uncarbonated phases, thereby inhibiting the continuation of the carbonation reaction further throughout the sample. When Fig. 4.10(a) and (b) were compared, it could be clearly seen that the main controlling factor in the strength development of RMC samples is the CO₂ concentration. Different from PC samples, which rely on the hydration process for strength gain, RMC samples depend on the carbonation reaction for the formation of a strength providing dense carbonate network (Unluer and Al-Tabbaa 2013, Unluer and Al-Tabbaa 2014). This takes place much slower in ambient CO₂ concentrations (0.04% CO₂), thereby leading to very low strengths when compared to accelerated carbonation (10% CO₂) conditions (i.e. 4 vs. 36 MPa at 28 days).

4.2.1.6 pH value

In RMC-based formulations, carbonation is a chemical reaction between brucite and CO₂, leading to the formation of HMCs, as shown in Equations 2.9-2.13. As carbonation involves a neutralizing process during which a reduction in the initially high pH value is expected (Johannesson and Utgenannt 2001, Sanchez, Gervais et al. 2002), the measurement of pH can indicate the extent of carbonation. However, differing from the carbonation of portlandite in PC-based samples, carbonation of brucite in RMC systems only leads to small changes in pH (Liska 2010). This is further supported with the lower solubility of MgO in comparison to CaO (~0.086 vs. ~1.73 g/l (Miller and Witt 1929, Kucera and Saboungi 1976)) and its incomplete hydration and carbonation.

Fig. 4.11 shows the pH values of selected RMC samples subjected to accelerated curing for up to 28 days in comparison to pure RMC and HMC (i.e. hydromagnesite) powders. Compared to the pH value of RMC (10.8), all samples indicated lower pH values that ranged between 10.4 and 10.6, which was an indication of carbonation. These values were higher than the pH of pure hydromagnesite (10.3), showing that the carbonation reaction was not fully completed. The presence of unreacted phases (i.e. MgO and Mg(OH)₂) was the main reason behind the slightly higher pH values of the RMC-based samples. The pH of carbonated samples generally decreased with the duration of carbonation and the inclusion of AEA, as expected, which could be attributed to the higher degree of carbonation within these samples over time.

Fig. 4.11 pH values of selected RMC samples subjected to accelerated carbonation

4.2.1.7 Crystal mineral components

Fig. 4.12(a) and (b) show the major phases of selected RMC samples subjected to accelerated and natural curing for up to 28 days via XRD patterns, respectively. Peaks of common HMCs such as nesquehonite and

hydromagnesite were observed in samples cured under accelerated carbonation. In addition to HMCs, the presence of unhydrated MgO and uncarbonated brucite peaks were also observed in all samples even after 28 days of accelerated carbonation. This was an indication of incomplete hydration and carbonation reactions within the time frames used in this study. Different from samples subjected to accelerated carbonation, the absence of HMC peaks in naturally cured samples shown in Fig. 4.12(b) indicated the lack of carbonation. This was also supported by the visible presence of unreacted brucite and MgO peaks within these samples.

(a)

(b)

Fig. 4.12 Major phases of selected RMC samples subjected to (a) accelerated carbonation and (b) natural curing via XRD patterns (M: Periclase; B: Brucite; H: Hydromagnesite; N: Nesquehonite)

Table 4.7 lists the relative contents of major phases of interest within these samples after accelerated carbonation and natural curing. A reduction in the residual MgO content was generally observed with curing age due to the continuation of the hydration reaction, which was accompanied with a corresponding increase in the brucite content over time. The main HMCs observed in most samples, hydromagnesite and nesquehonite, generally increased in content with curing duration, indicating an increase in the carbonation degree. The influence of AEA inclusion was also observed via a comparison of M0.56 and MA0.56 samples over different curing durations. The phase quantification results indicated up to ~60% higher contents of carbonate phases within samples containing AEA at different durations. This was an indication that the inclusion of AEA within RMC formulations facilitated carbonation. Therefore, the increase in the porosity of samples containing AEA was compensated by the extensive formation of HMCs within these samples, as also previously confirmed by the strength results.

Table 4.7 Quantification of major phases in samples subjected to accelerated carbonation and natural curing calculated via XRD Rietveld analysis

Sample	Age (days)	MgO (wt.%)	Brucite (wt.%)	Nesquehonite (wt.%)	Hydromagnesite (wt.%)	Total HMCs (wt.%)
M0.56-A	7	31.6	54.4	2.8	11.3	14.1
M0.56-A	14	29.8	56.6	2.5	11.1	13.6
M0.56-A	28	23.0	61.4	2.6	13.0	15.6
MA0.56-A	7	34.1	47.3	4.9	13.7	18.6
MA0.56-A	14	32.8	45.9	6.9	14.4	21.3
MA0.56-A	28	30.7	48.0	6.4	15.0	21.4
MA0.69-A	7	12.5	71.3	6.1	10.2	16.3
M0.56-N	28	16.9	80.6	0.2	2.3	2.5
MA0.56-N	28	20.0	76.6	0.2	3.3	3.5

The influence of water content was assessed via a comparison of MA0.56

and MA0.69 samples cured under accelerated carbonation for 7 days. The lower residual MgO content within MA0.69 was attributed to its higher water content, enabling higher degrees of hydration. This corresponded well with the higher brucite content of this sample. However, the presence of water slowed down the diffusion of CO₂ and resulted in lower carbonation degrees, which was evident from the lower HMC content of MA0.69 when compared to the corresponding MA0.56 sample. Although water acts as a medium for hydration and carbonation reactions, excessive water in pores can block the diffusion of CO₂ and inhibit the further carbonation of RMC samples. The excessive water also led to higher porosities as shown earlier, which can result in lower strengths in the absence of necessary carbonation. These results were in line with the previous literature (Liska, Vandeperre et al. 2008) and the strength results reported earlier, indicating the lower strengths obtained in the presence of higher water contents due to limited carbonation.

The effect of natural curing as opposed to accelerated carbonation was clear from the higher uncarbonated brucite contents (up to 81% vs. 61%). However, the lower residual MgO contents of the naturally cured samples (up to 20% vs. 31%) were an indication of higher hydration degrees in the absence of CO₂ curing. Regardless of the increase in the extent of hydration, the lack of carbonation within these samples revealed much lower HMC contents, which led to negligible strength gain. Similar to accelerated carbonation, the presence of AEA led to a slight increase in the HMC content of naturally cured samples, albeit not being effective in terms of strength development. These results highlight the importance of CO₂ concentration and the progress of carbonation on the final mechanical performance of RMC-based formulations.

4.2.1.8 Carbon sequestration

The mass loss of selected RMC samples subjected to accelerated and natural curing via TGA/DSC curves is presented in Fig. 4.13(a) and (b), respectively. Three major decomposition steps in accordance with the previous literature

(Frost, Bahfenne et al. 2008, Vágvölgyi, Frost et al. 2008, Hollingbery and Hull 2010, Jauffret, Morrison et al. 2015, Purwajanti, Zhou et al. 2015) were identified as:

(i) 40 to 300 °C: Dehydration of water bonded to HMCs (Vágvölgyi, Frost et al. 2008, Jauffret, Morrison et al. 2015, Purwajanti, Zhou et al. 2015).

(ii) 300 to 500 °C: Dehydroxylation of HMCs (e.g. nesquehonite and hydromagnesite), decarbonation of HMCs (e.g. nesquehonite) and decomposition of uncarbonated brucite (Hollingbery and Hull 2010, Jauffret, Morrison et al. 2015).

(iii) 500 to 900 °C: Decarbonation of HMCs (e.g. nesquehonite and hydromagnesite) (Jauffret, Morrison et al. 2015).

(a)

(b)

Fig. 4.13 Mass loss of selected RMC samples subjected to (a) accelerated carbonation and (b) natural curing via TGA/ DSC curves

Table 4.8 lists the a summary mass losses associated with the H₂O and CO₂ contents within selected RMC samples at each stage of thermal decomposition. Along with the total mass loss values, the percentage mass loss corresponding to the loss of H₂O from the decomposition of brucite was determined via XRD analysis and subtracted from the total mass loss observed between 300 and 500 °C during TGA to determine the mass loss due to the decomposition of HMCs.

Table 4.8 A summary of quantification of H₂O and CO₂ calculated by TGA in RMC samples after accelerated carbonation and natural curing

Sample	Age (days)	Weight loss (wt.%)					
		<300 °C	300- 500 °C	500- 900 °C	H ₂ O (brucite)	CO ₂	Total
M0.56-A	7	8.1	27.1	4.9	16.9	15.1	40.1
M0.56-A	14	9.9	26.5	5.7	17.6	14.7	42.2
M0.56-A	28	8.8	27.6	6.6	19.0	15.2	43.1
MA0.56-A	7	10.5	26.1	5.0	14.7	16.4	41.6
MA0.56-A	14	10.2	27.9	4.6	14.2	18.3	42.7
MA0.56-A	28	11.2	28.6	4.7	14.9	18.4	44.5
MA0.69-A	7	7.3	25.8	6.4	22.1	10.1	39.5
M0.56-N	28	1.8	22.5	6.0	25.0	3.5	30.3
MA0.56-N	28	1.6	21.6	5.8	23.8	3.6	29.0

The results obtained were in line with the XRD quantification and compressive strength measurements. The total mass loss revealed by all samples increased with curing duration under accelerated carbonation and with the introduction of AEA. The increase of water content from 0.56 to 0.69 observed via a comparison of samples M0.56-A and M0.69-A indicated an increase in

brucite content due to the availability of a higher amount of water molecules that enabled the continuation of the hydration reaction. However, this was accompanied with reduced carbonation and lower CO₂ contents as observed and explained earlier, which corresponded well with the strength results.

The quantification results show that a small increase in the CO₂ content was generally observed with an increase in the curing duration from 7 to 28 days under accelerated carbonation, indicating that a majority of the carbonation reaction took place within the first 7 days of curing. The introduction of AEA led to > 20% increase in the CO₂ captured within most of the samples, highlighting the role of entrained air in the enhancement of CO₂ sequestration within RMC formulations. In line with the findings revealed in Section 4.2.1.7, samples subjected to natural curing demonstrated lower CO₂ contents than those cured under accelerated carbonation (~4% vs. 15-18%) due to the low CO₂ concentrations under ambient conditions. This low carbonation was accompanied with higher brucite contents that remained uncarbonated. Different from accelerated carbonation, the introduction of AEA did not play a major role in the increase of carbonation under natural curing conditions, indicating the necessity for the availability of higher CO₂ concentrations for the continuation of carbonation and associated strength gain within a few days.

4.2.1.9 Microstructure

Mix design and penetrability of CO₂ were identified as two of the main factors that influence the carbonation process of RMC formulations and the formation of various carbonate phases (Liska and Al-Tabbaa 2012, Unluer and Al-Tabbaa 2013, Unluer and Al-Tabbaa 2014). Fig. 4.14 shows the microstructural images of selected RMC samples via scanning electron microscope to reveal the influence of different curing conditions (accelerated carbonation vs. natural curing) and the presence of AEA on the microstructure of RMC samples. An abundant formation of rosette-like hydromagnesite (diameter ~0.8 µm, thickness < 0.1 µm) was observed in both the M0.56-A

and MA0.56-A samples subjected to accelerated carbonation for 14 days, regardless of the presence of AEA. This can explain the comparable performance of these samples, revealed by their similar compressive strengths at 14 days. However, the introduction of AEA also led to the formation of needle-like nesquehonite (length $\sim 1.0\ \mu\text{m}$, width $\sim 0.9\ \mu\text{m}$), as observed in Fig. 4.14(d). The nesquehonite formation was also shown in the phase quantification results listed in Table 4.7 and can be linked to the influence of AEA in enhancing the diffusion of CO_2 within RMC samples. This led to increased carbonation enabled by the formation of different carbonate phases.

Fig. 4.14 Microstructural images of selected RMC samples subjected to accelerated carbonation: (a) M0.56-A (14 days, x10000); (b) M0.56-A (14 days, x50000); (c) MA0.56-A (14 days, x10000); (d) MA0.56-A (14 days, x50000); (e) M0.56-N (28 days, x10000) via scanning electron microscope

The co-existence of HMCs, which facilitate microstructural strength development in RMC formulations due to their strong, fibrous, acicular or otherwise elongated nature via the interlocking effects occurring between the crystals; has been observed in previous studies (Mo and Panesar 2012, Mo and Panesar 2013, Unluer and Al-Tabbaa 2013, Unluer and Al-Tabbaa 2014). The overall sample performance is determined by the compact and interlocked network-like structure provided by interconnected and well-developed carbonate crystals (De Silva, Bucea et al. 2006). Fibrous and needle-like crystal growths provided by carbonate phases such as nesquehonite are more beneficial than rounded or tabular crystals due to the formation of 3D structures. Nesquehonite is prismatic and forms star-like clusters, whereas hydromagnesite is comprised of rounded rosette-like crystals. The elongated morphology of nesquehonite reduces porosity and improves stiffness by raising the solid volume by a factor of 2.34 upon its conversion from brucite.

In this study, the formation of nesquehonite with the introduction of AEA in sample MA0.56-A may have compensated the strength loss caused by the introduction of air voids. The entrained air voids are generally interconnected by the capillary porosity, although they may appear to be relatively isolated in some microstructural images. Therefore, the use of AEA can lead to an increase in gaseous diffusivity and permeability by a factor of up to 2-3, depending on the mix design (Wong, Pappas et al. 2011). This has been reflected by the increased diffusivity and penetration of CO₂ through the AEA-containing samples investigated under this study, leading to higher carbonate contents revealed by XRD, TG and SEM analyses.

Unlike those subjected to accelerated carbonation, samples subjected to natural curing presented the widespread presence of uncarbonated brucite and unhydrated MgO in Fig. 4.14 (e). The absence of carbonate phases can explain the lower strength results obtained by the naturally cured samples.

4.2.1.10 Thermal conductivity

Table 4.9 presents the thermal conductivity of selected RMC samples at different curing ages. An increase in thermal conductivity was generally observed with age in line with the increased density of samples as carbonation proceeded over time. The increase in the air content via the introduction of AEA in MA0.56 led to a noticable (15-22%) reduction in its thermal conductivity at all ages. This is because the thermal conductivity of cement-based samples is mainly affected by mix design and the presence of air amongst the interconnected voids. As air is resistant to heat flow (0.024 W/m·K at standard atmosphere), a majority of the heat is conducted via the solid phases (Wong, Glasser et al. 2007).

Table 4.9 Thermal conductivity of selected samples subjected to accelerated carbonation at different curing ages

Sample / Thermal conductivity (W/m·K)	Age			
	1 day	7 days	14 days	28 days
M0.56-A	1.31	1.45	1.50	1.51
MA0.56-A	1.11	1.13	1.22	1.20
M0.69-A	-	-	-	1.20
MA0.69-A	-	-	-	1.16

The influence of water content on thermal conductivity was studied via a comparison of the M0.69-A and M0.56-A samples. The results indicated a reduction in thermal conductivity with an increase in water content. Similar findings were reported in an earlier study (Wong, Glasser et al. 2007), which theoretically and experimentally showed that cement samples with a w/b ratio of 0.35 indicated much lower thermal conductivity values than corresponding samples with a w/b of 0.25. This is mainly because higher water contents lead

to higher capillary porosities, increasing the resistance of concrete samples to heat flow. The similar thermal conductivity values of samples MA0.56-A and M0.69-A at 28 days also indicates the comparable effect of the introduction of AEA and increased water contents on the thermal conductivity of the prepared samples.

4.2.2 Conclusion

1. The workability of RMC samples with lower water contents was significantly improved with the use of AEA as the introduced air voids acted as air cushions between particles, thereby reducing friction and interlocking.

2. The use of AEA generally led to lower strength results during the early ages due to the initially increased air contents of the samples it was incorporated in. However, this increase in air content was compensated by the increase in the diffusivity and penetration of CO₂ through the pore network. The increased diffusion of CO₂ led to higher carbonation degrees and increased strength gain in RMC samples, which relied on the availability and diffusion of CO₂ through their pore network via the accelerated carbonation process for strength gain. Therefore, RMC samples containing AEA revealed similar strength results as corresponding samples without AEA at 28 days.

3. In addition to the increase in the diffusivity and penetration of CO₂ through the pore network, another factor that controlled the degree of carbonation was the CO₂ concentration used during the curing process. An increase in the CO₂ concentration from ambient (0.04%) to 10% led to significantly higher strengths due to the dense formation of carbonate phases in RMC samples. This was because RMC samples relied on the progress of carbonation and the dense formation of carbonate phases for strength gain.

4. The quantification of the hydrate and carbonate phases after the curing process indicated the beneficial use of AEA in increasing the amount of total carbonate phases and facilitating the formation of nesquehonite alongside hydromagnesite. The simultaneous formation of these HMCs contributed to strength gain in RMC samples. This was associated with the increased rate of CO₂ diffusion within these samples, which was enabled with the development of an interconnected air network via the use of AEA. Furthermore, the increase in the air content with the introduction of AEA resulted in the reduction of the thermal conductivity of RMC samples. This improvement in thermal conductivity was related to the high resistance of air voids to heat flow. A similar effect was observed with the increase in the initial water content, which was associated with the increased capillary porosity of the designed formulations.

4.3 Influence of different replacements of industrial by-products (i.e. pulverized fuel ash (PFA) and ground granulated blast furnace slag (GGBS)) on the mechanical and carbon sequestration of RMC formulations

4.3.1 Results and discussion

4.3.1.1 Porosity

Fig. 4.15 shows the porosities of RMC samples and PC samples during the 28 days of CO₂ curing and natural curing. While the porosity of the PC sample (P40) remained stable at ~10-12% during the entire course of curing, RMC and RMC-SCM samples indicated a decrease in their porosities associated with the different curing conditions they were subjected to (i.e. sealed vs. carbonation). The initial porosity of the RMC control sample (M40) before carbonation was 31%, whereas those containing SCMs ranged between 22-27%, partially attributed to the variations within the initial water contents of these formulations. In addition to the reduction in porosity with the introduction of SCMs, the progress of carbonation and the expansive formation of

carbonate phases within the pore space led to denser microstructures in these samples (Unluer and Al-Tabbaa 2013, Unluer and Al-Tabbaa 2014). The reduction in porosity was most prominent during the first 7 days of curing, which was in line with the rate of carbonation that usually slows down after a few days due to the reduction in the diffusion rate of CO₂. The formation of HMCs within RMC and RMC-SCM samples reduced the porosity levels all the way down to 6-10%, revealing similar final porosity levels with that of the PC sample at the end of 28 days.

Fig. 4.15 Porosities of RMC samples and PC samples during the 28 days of CO₂ curing and natural curing

In comparison to the RMC control sample (M40), the use of SCMs in RMC formulations led to lower porosity values at all times. This could be partially attributed to the formation of hydrate phases such as M-S-H and hydrotalcite due to the reaction between RMC and PFA/GGBS, leading to a reduction in the overall porosity as observed in previous studies (Yi, Liska et al. 2014). Furthermore, the “filler effect” associated with the small particle sizes of these SCMs could have contributed to the densification of the sample

microstructure by filling in the gaps in-between the larger RMC agglomerates (Lammertijn and De Belie 2008). This effect can be observed via a comparison of the porosities of the RMC and RMC-SCM samples before carbonation (i.e. on day 0). Samples containing PFA revealed lower porosities than those containing GGBS at both replacement levels, whereas the porosity decreased with an increase in the amount of PFA that replaced RMC. This could be due to the more pronounced filler effect achieved by the PFA particles as well as the extent of the hydration reaction within the RMC-PFA system.

4.3.1.2 Water sorptivity

Measurements of water sorptivity were performed to assess the capillary suction of unsaturated concrete samples with different compositions when placed in contact with water. The results obtained by this measurement could be an indication of the carbonation ability of each sample as water ingress could reflect the pore structure and provide an indirect measurement of interconnected capillary pores (Basheer, Kropp et al. 2001). The main output of this test was the initial rate of water absorption of samples before and after 7 days of curing, as reported in Fig. 4.16.

Fig. 4.16 Water sorptivities of RMC samples before and after 7 days of CO₂ curing and PC samples before and after 7 days of natural curing

All samples experienced a significant reduction in their water sorptivity values after hydration and carbonation due to the densification of their microstructures. This was enabled via the formation of hydrate and carbonate phases during the measured time frame. In comparison with RMC and RMC-SCM samples, PC samples indicated a much lower water sorptivity before the curing process, which was in line with the porosity values presented in Fig. 4.15. This difference between the sorptivity values of RMC and PC samples greatly diminished after curing. The progress of hydration within the PC samples led to a slight reduction in their capillary pore space over time, thereby reducing their water sorptivity; whereas the RMC and RMC-SCM samples indicated significant reductions associated with carbonation curing.

Similar to the porosity measurements, the RMC control sample (M40) revealed the largest water sorptivity value amongst all samples before curing. The inclusion of PFA led to reduced water sorptivity, which reduced further with increasing PFA content. Samples containing the highest PFA content (M20-F20) achieved the lowest values before curing, whereas the replacement of RMC with GGBS only slightly reduced the sorptivity values. Samples M30-G10 and M20-G20 containing two different GGBS contents revealed similar water sorptivities, independent of the GGBS content. A comparison of RMC-PFA and RMC-GGBS samples, whose w/b contents were identical, can indicate the influence of PFA in reducing the initial porosities of RMC samples.

Subjecting these samples to carbonation for 7 days led to a visible 67-95% reduction in their water sorptivity, which could be attributed to the expansive formation of hydrate and carbonate phases within the pore system. When compared to M40, the reduced initial sorptivity values of RMC-SCM samples before curing, which was associated with the finer particle sizes (i.e. filling effect) of the SCMs and the lower water contents of these samples, led to slightly lower reductions due to carbonation, which could indicate the smaller

degree of carbonation within these samples in comparison to M40. The lower carbonation degrees observed within the RMC-SCM samples was as expected since these samples had lower initial porosities and RMC contents than M40, both influencing the progress of carbonation.

4.3.1.3 Compressive strength

Fig. 4.17 shows the compressive strength of RMC samples under CO₂ curing and PC samples under natural curing for up to 28 days. A steady strength development associated with the progress of carbonation was generally observed in all RMC and RMC-SCM samples. The 28-day strength of these samples varied between 37 and 60 MPa, during which the strength of the PC sample was reported as 55 MPa. These results were a clear indication of the ability of RMC samples in achieving similar or higher strengths than corresponding PC samples when the right curing conditions were provided. The strength gain demonstrated by RMC samples was due to the reaction of hydrate phases with CO₂, leading to the growth of a dense HMC network (Dung and Unluer 2016); whereas PC samples relied on the hydration process and the formation of hydrate phases such as C-S-H for strength gain (Rostami, Shao et al. 2012).

Fig. 4.17 Compressive strengths of RMC samples under CO₂ curing and PC samples under natural curing for up to 28 days

The effect of PFA inclusion on the performance of RMC samples could be assessed via a comparison of the control (M40) with the M30-F10 and M20-F20 samples, in which the PFA content was 0%, 25% and 50% of the total binder content. The use of increased PFA contents led to a slight reduction in the initial (≤ 14 days) strength values, which could be attributed to the lower carbonation rates within these samples due to their lower RMC contents and reduced porosities, which could slow down the diffusion of CO_2 through the sample. However, a different scenario was observed in the longer-term strength development of these samples. While the M40 sample achieved a final strength of 45 MPa without the use of any SCMs, the inclusion of PFA led to 33% higher strengths and reached 60 MPa. The improvement in the 28-day strength values was directly correlated with the PFA content and was therefore more pronounced in the M20-F20 sample, in which half of the RMC was replaced with PFA. This improvement in the performance of the M20-F20 sample was in agreement with the reduction of porosity presented in Fig. 4.15, where this sample demonstrated the lowest porosity amongst all samples at the end of 28 days. This reduction in porosity and associated increase in strength were not only enabled by the filler effect facilitated by the inclusion of PFA, but also the hydration and carbonation reactions within the pore solution. Within RMC-PFA systems, the formation of M-S-H and hydrotalcite can be observed via the reaction between SiO_2 , Al_2O_3 and Mg-phases; accompanied with the formation of HMCs via the carbonation of Mg-phases. A similar reaction mechanism was reported in earlier studies (Vandeperre, Liska et al. 2008, Jin, Gu et al. 2013, Jin, Gu et al. 2015), where the ability of MgO to activate PFA and enable the formation of strength providing phases such as M-S-H and hydrotalcite was revealed.

Unlike PFA-based samples, the inclusion of GGBS at the same rates as PFA (i.e. 25% and 50% of the total binder content) within samples M30-G10 and M20-G20 led to a reduction in the strength of RMC samples. Although the high CaO and SiO_2 contents within GGBS could have led to the formation of C-S-H via its activation in the presence of MgO (Jin, Gu et al. 2013), the

carbonation conditions these samples were cured under may have led to the conversion of C-S-H into calcite and silica (Borges, Costa et al. 2010), which can explain the observed reduction in strength. The RMC within these samples was also not enough to fully compensate for the strength loss associated with the conversion of C-S-H due to its low content available for carbonation. The overall degree of carbonation could have been further hindered because of the lower initial porosities of these samples, owing to the finer particle size of GGBS, which presented a lower permeability for CO₂ diffusion (Shi, Xu et al. 2009). The similar porosities of M30-G10 and M20-G20 throughout the entire curing period was reflected in their identical strength development, in which both samples revealed similar strengths at all durations. These results clearly highlight the important role mix design and sample porosity play during the carbonation and associated strength gain of RMC formulations.

4.3.1.4 Thermal conductivity

The thermal conductivity values of RMC samples after 7 days of CO₂ curing and PC samples after 7 days of natural curing are presented in Fig. 4.18. When compared to the RMC control sample (M40), which demonstrated a higher thermal conductivity than the PC sample (P40), the inclusion of PFA and GGBS led to a reduction in the thermal conductivity values of all samples. These RMC-SCM samples achieved similar or lower thermal conductivities than P40, which could be due to the reduction in the dry unit mass of the RMC sample with the introduction of SCMs (Blanco, García et al. 2000). Furthermore, the amorphous structure of PFA and GGBS may have also contributed to the decrease in the thermal conductivity of these samples. Overall, these results indicate the improvement in the thermal conductivity values of RMC samples with the introduction of SCMs, which can achieve similar values to those of PC samples.

Fig. 4.18 Thermal conductivities of RMC samples after 7 days of CO₂ curing and PC samples after 7 days of natural curing

4.3.1.5 Microstructure

Sample M20-F20, which outperformed all other samples at 28 days, was further analyzed for the identification of phases that formed during the curing process. Fig. 4.19 shows the microstructural image and elemental analysis of M20-F20 after 28 days of 10% CO₂ curing via scanning electron microscope. The clear formation of rosette-like hydromagnesite/dypingite as the main carbonate phase was observed in the SEM image. The dense structure of the formed carbonate phase corresponded well with the strength development of this sample. In addition to the presence of carbonate phases, elemental analysis indicated the presence of silica, which could be linked with the use of PFA and potential formation of M-S-H, as reported in previous studies (Abdalqader, Jin et al. 2015).

Fig. 4.19 Analysis of sample M20-F20 at 28 days of CO₂ curing via (a) SEM and (b) EDX

This study focused on the use of two common SCMs, PFA and GGBS, as a cement replacement and reported their influence on several performance and environmental aspects of RMC-based concrete formulations. The performance related results indicated a stable trend in the porosity of PC samples throughout the curing process, whereas a significant reduction in the porosities and water sorptivities of RMC, RMC-PFA and RMC-GGBS samples was observed due to the carbonation process

4.3.2 Conclusion

1. The performance related results indicated a stable trend in the porosity of PC samples throughout the curing process, whereas a significant reduction in the porosities and water sorptivities of RMC, RMC-PFA and RMC-GGBS samples was observed due to the carbonation process. When compared to PC samples, the higher initial porosities of RMC samples were related to the higher water demand of RMC as well as the presence of agglomerates within its structure, which contributed to the diffusion of CO₂ within the sample pore system. The densification of the microstructures of these samples during the curing process was associated with the expansive formation of a dense carbonate network, which was the main source of strength gain.

2. Since the final strength of RMC samples was determined by the compact and interlocked network-like structure provided by interconnected and well-developed carbonate crystals, the extent of the carbonation reaction, which depended on the mix design and well as the binder properties, determined the performance of these samples.

3. While the use of both PFA and GGBS in RMC samples led to smaller initial porosity and water sorptivity values due to their finer natures, RMC-PFA samples achieved the lowest porosity values amongst all samples at the end of 28 days. This reduction in the porosity of RMC samples was in agreement with their steady strength development that led to 28-day strength values of

45 MPa, which were lower than those obtained by PC samples via hydration (55 MPa). However, the introduction of PFA in RMC formulations revealed higher strengths (60 MPa) than both the RMC and PC samples. These improvements were associated with the densification of samples containing PFA or GGBS because of the filler effect as well as the pozzolanic reactions that led to the formation of hydrate phases, thereby reducing the initial porosity. Accordingly, the strength enhancement, which was most pronounced in the RMC-PFA sample, translated into the lowest final porosity due to the filler effect of PFA and the formation of strength providing Mg-bearing hydrate and carbonate phases during carbonation curing.

4.4 A summary of key conclusions in this chapter

The initial water content was determined as the main parameter controlling the final properties of RMC samples, which demonstrated a substantial increase in their density and an associated decrease in porosity over 28 days. Meanwhile, the final strength of RMC samples was also determined by the compact and interlocked network-like structure, rather than their quantity, provided by interconnected and well-developed carbonate crystals, the extent of the carbonation reaction, which depended on the mix design and well as the properties of binders containing industry waste and air-entrained agents. The densification of the microstructures of these samples during the curing process was associated with the expansive formation of a dense carbonate network, which was the main source of strength gain.

Chapter 5 INTRODUCTION OF CALCINED DOLOMITE AS A NEW RMC SOURCE

The environmental impacts are low in terms of the production of reactive magnesia, however, its cost is much higher compared with that of PC, therefore, it is necessary to find alternative magnesia source with a low expense. Dolomite has been proposed as it is an industry waste, which is usually used as coarse aggregates in concrete.

This chapter consisted of two main sections, which focused on the introduction of calcined dolomite in RMC formulations. The first study investigated the performance and microstructural development of RMC mixes containing various contents of dolomite calcined at 800 °C (D800) under carbonation curing for up to 28 days. The performance of each sample was assessed via compressive strength testing, which was linked with the hydration and carbonation mechanisms studied via isothermal calorimetry, XRD, TGA/DSC and SEM-EDX analyses. The mix designs used in this part are shown in Table 3.9.

This was followed by the second part of the study focusing on the investigation of strength and microstructural development of two magnesium-based binders (i.e. RMC and dolomite calcined at different temperatures) under different curing conditions. Compressive strength testing was used to evaluate the mechanical properties of samples through the variation of temperature and relative humidity. Isothermal calorimetry, XRD, TGA/DSC and SEM-EDX analyses were used to investigate the extent of hydration and carbonation of each sample. Table 3.10 presents the mix designs used in this part.

5.1 Influence of various contents of calcined dolomite replacements on the mechanical performance and carbon sequestration of RMC formulations

5.1.1 Results and discussion

5.1.1.1 Isothermal calorimetry

The heat flow and cumulative heat of all pastes are shown in Fig. 5.1(a) and (b), respectively. The RMC-based control sample M demonstrated a high initial heat flow peak at < 1 hour due to the high reactivity of MgO. A reduction in the intensity and occurrence time of the initial peak was observed with the introduction of dolomite into samples M75D25, M50D50, M25D75 and D800, whose highest peaks were revealed between 1.9 and 4.3 hours of hydration. The heat flow of all samples reduced with increasing dolomite content, which could be partially attributed to the decrease in the hydration degree because of the common ion effect due to the presence of CaO along with MgO within these samples. Furthermore, the reduction in the peak intensity and cumulative heat was also associated with the decreasing initial MgO (i.e. the main binder phase) contents in samples with high dolomite contents. This could explain the highest heat flow peak as well as the largest amount of cumulative heat exhibited by the control sample M. Alternatively, the presence of calcite within samples containing dolomite increased the surface area available for hydration by enabling the nucleation of hydrate phases on calcite surfaces, thereby increasing the accessibility of the MgO particles for hydration at early stages. The nucleation effect increased with increasing calcite content, which was demonstrated by the leftward shift in the heat flow peak from 4.3 hours in sample M75D25 to 1.9 hours in D800. Therefore, the overall hydration process of RMC and dolomite-based samples mainly depended on the interplay between the MgO and dolomite (i.e. MgO, CaO and CaCO₃) contents within the initial mix design.

(a)

(b)

Fig. 5.1 Isothermal calorimetry results showing (a) heat flow and (b) cumulative heat of all samples

5.1.1.2 Porosity

The porosities of all samples under 10% CO₂ curing for up to 28 days are shown in Fig. 5.2. A reduction in the porosities of all samples was observed over time, which was associated with the formation of hydrate and carbonate phases during the curing process. The initial porosity values before carbonation ranged between 15-31%. While the control sample M revealed the highest initial porosity, an increase in the dolomite content led to a

consistent reduction in the initial porosity values. Differences in these values were associated with variations in the initial water contents, and thereby the available capillary pore space, which decreased with increasing dolomite content, leading to lower porosities.

Fig. 5.2 Porosities of all concrete samples under 10% CO₂ curing for up to 28 days

The use of carbonation curing reduced the initial porosities from 15-31% to 6-10% over 28 days. Under continuous exposure to CO₂, the expansive formation of HMCs within the pore system resulted in the reduction of the initially available porosity, as reported in previous studies (Mo and Panesar 2012, Unluer and Al-Tabbaa 2013, Unluer and Al-Tabbaa 2014). The initially fast reduction in the porosity of all samples was followed by a gradual decrease after 7 days, which was associated with the progress of carbonation within the sample pore system (Ruan and Unluer 2017, Ruan and Unluer 2017). This decrease in the carbonation rate over time could be associated with the reduction of the initial porosity via its occupation by a dense carbonate layer, which slowed down the diffusion of CO₂ within the pore

space and hindered its access to uncarbonated phases (Harada, Simeon et al. 2015). When the final (i.e. 28-day) porosities of all samples were compared, the porosities of samples containing dolomite ranged between 6-8%, whereas the control sample M, without any dolomite content, revealed a higher porosity of 10%. While the extent of the reduction in the overall porosities of each sample over time could reflect their carbonation capabilities and associated strength gain, the final porosities achieved by each sample were also considered in the subsequent assessment of their performance.

5.1.1.3 Compressive strength

Fig. 5.3 illustrates the compressive strength of all concrete samples subjected to accelerated carbonation for up to 28 days. Samples with low dolomite contents, M and M75D25, achieved compressive strengths of up to 20 MPa after only 3 days of curing. These were followed by M50D50, whose corresponding strength gain was limited to 7 MPa, accounting for 35% of the strength of the control sample M subjected to the same period of curing. Although samples containing higher dolomite contents revealed low strengths at early stages, they demonstrated a continuous strength gain over the 28 days of curing. The delayed strength gain of these samples could be partially attributed to their relatively higher water/MgO ratios included within the initial mix design, which could slow down the diffusion of CO₂ within the pore system and reduce the degree of carbonation. Furthermore, as revealed by the porosity measurements, the presence of carbonate phases in dolomite could result in a lower initial porosity via the formation of a carbonate layer, which could inhibit the ingress of CO₂ within the pore system (Mo and Panesar 2012).

Alternatively, the control sample M with the highest RMC and no dolomite content achieved high strengths at early ages, whereas its strength development was almost completed in 14 days. In comparison, although sample D800 containing only dolomite revealed low strengths at early ages, it demonstrated similar strengths as sample M after 14 days of curing. The

lower strengths of D800 than those of samples including RMC and dolomite was attributed to its high water/MgO ratio as well as its low initial porosity, which limited the degree of carbonation and thereby the formation of strength providing HMCs. The strength development of D800 over time (i.e. between 3 and 14 days) could be enhanced by the presence of carbonates that acted as nucleation sites and participated in the formation of a dense carbonate network.

Fig. 5.3 Compressive strength of all concrete samples subjected to accelerated carbonation for up to 28 days

Samples that incorporated the simultaneous use of RMC and dolomite (M75D25, M50D50 and M25D75) demonstrated a continuous strength gain and achieved strengths as high as 57 MPa at 28 days, which was 46% higher than sample M, whose 28-day strength was limited to 39 MPa. The higher strengths achieved by these samples were attributed to the presence of calcite, which enabled higher reaction degrees by providing nucleation sites

for the continuous formation of hydrate and carbonate phases and contributing to the formation of a dense carbonate network. The trends observed in the strengths of these samples in comparison to the control sample were also in line with the final porosity results shown in Fig. 5.2, where the smaller 28-day porosities of M75D25, M50D50 and M25D75 were demonstrated. Amongst all samples, the highest strengths achieved by samples M75D25 and M25D75 revealed the interplay between the MgO and dolomite contents as both contributed to strength development. While higher contents of MgO enabled early strength gain, the presence of undecomposed carbonate phases contributed to the formation of a dense carbonate network and facilitated the continuation of the carbonation reaction via the provision of additional nucleation sites. These improvements in the reaction mechanisms led to a continuous strength gain with the extensive formation of a carbonate network.

5.1.1.4 Crystal mineral components

Fig. 5.4 shows the major phases within all samples after 28 days of 10% CO₂ curing via XRD patterns. Peaks corresponding to MgO, brucite and calcite as well as HMCs such as hydromagnesite and nesquehonite could be observed. The presence of HMCs was a clear indication of the progress of carbonation throughout the curing process, whereas the residual MgO and brucite peaks revealed the incomplete hydration and carbonation reactions, respectively. The most prominent HMC observed was hydromagnesite, accounting for more than 95% of the HMCs in all samples. Hydromagnesite was accompanied with minor amounts of nesquehonite in dolomite-based samples. The overwhelming formation of hydromagnesite over nesquehonite could be explained by their different water/MgO mass ratios of around 0.5 and 1.4, respectively. As the water/MgO ratios of the samples prepared in this study ranged between 0.6 and 0.8 for RMC-based samples and 1.0 for D800, the formation of hydromagnesite was generally favored over nesquehonite. In addition to the HMCs, the calcite peaks observed in all samples except for the control sample M were due to the presence of dolomite.

Fig. 5.4 Major phases within all samples after 28 days of 10% CO₂ curing via XRD patterns (M: Periclase B: Brucite C: Calcite H: Hydromagnesite N: Nesquehonite)

The phase quantification results listed in Table 5.1 clearly distinguished each sample in terms of their MgO, brucite, calcite and HMC contents. These were further supported with the carbonation degree of each sample, which was quantified by structure refinement via Rietveld analysis. An increase in the carbonation degree of MgO was observed with an increase in the calcite content. Sample D800 revealed the lowest residual MgO and brucite contents, whose high consumption degree in the carbonation reaction led to a high carbonation degree (90%). This was not only due to the initially low MgO content of D800 when compared to other RMC-based samples, but also the presence of calcite that enabled the continuation of the hydration and carbonation reactions. Accordingly, the absence of calcite, combined with its high initial MgO content, led to abundant amounts of unreacted MgO and brucite in sample M, thereby revealing a lower carbonation degree (25%).

Table 5.1 Phase quantification results of all samples after 28 days of 10% CO₂ curing

Sample	Content (wt. %)					Carbonation degree (%)
	MgO	Brucite	Nesquehonite	Hydromagnesite	Calcite	
M	23.7	34.9	0.0	37.2	1.4	25.1
M75D25	9.6	19.5	1.7	53.3	14.0	50.4
M50D50	6.6	13.2	1.9	50.4	26.5	58.6
M25D75	3.5	6.4	1.5	48.7	40.3	73.0
D800	1.5	0.5	1.9	38.3	57.7	90.0

The low amounts of MgO and brucite present within the dolomite sample D800 was an indication of the insufficient binder content available for carbonation within this sample, which could explain its limited strength development when compared to other samples. On the other hand, sample M with the highest initial MgO content achieved a low carbonation degree (25%), owing to the absence of nucleation sites that could provide additional surface area for the formation of hydrate and carbonate phases. In the absence of nucleation sites, the precipitation of these phases on unreacted MgO and brucite particles could slow down the degree of reaction by forming a layer of hydration and carbonation products that prevented further access to these particles. A comparison of the control sample M and M75D25 revealed the doubling of the carbonation degree from 25% to 50%, which was partially attributed to the nucleation effect provided by calcite present within M75D25, along with its lower initial MgO content readily available for hydration and carbonation.

Samples that incorporated dolomite and RMC within the initial mix design (M75D25, M50D50 and M25D75) not only revealed much lower residual MgO and brucite contents than sample M, but also indicated significantly higher carbonation degrees. The high HMC contents of these samples at 28 days, which were generally > 50%, could explain the lower final porosities and

improved strength results they demonstrated in comparison to the control samples M and D800. While samples M and D800 revealed similar 28-day strengths of 36-39 MPa albeit their different water contents, samples incorporating RMC and dolomite (M75D25, M50D50 and M25D75) led to much higher corresponding strengths of 48-57 MPa. These results clearly indicate the critical role the carbonation reaction and associated formation of HMCs play in determining the final performance of RMC and dolomite-based concrete formulations.

5.1.1.5 Carbon sequestration

Fig. 5.5 shows the weight loss of all samples after 28 days of 10% CO₂ curing via TGA/DSC curves. The decomposition reactions and their corresponding temperature ranges observed within the RMC and dolomite samples are summarized in Table 5.2. The three main temperature ranges identified were 50-300, 300-500 and > 500 °C. The initial step involved the dehydration of HMCs (i.e. hydromagnesite and nesquehonite), which took place between 50-300 °C. Hydromagnesite lost 4 water molecules in a single endothermic peak, while nesquehonite dehydrated in 3 steps, losing one water molecule at each step during the 3-step dehydration process (Sawada, Uematsu et al. 1978, Padeste, Oswald et al. 1991, Hales, Frost et al. 2008, Ferrini, De Vito et al. 2009, Hollingbery and Hull 2010, Jauffret, Morrison et al. 2015). Overlapping peaks between the temperature range of 300-500 °C corresponded to the decomposition of uncarbonated brucite (i.e. endothermic peak at ~400 °C) and dehydroxylation of HMCs (i.e. endothermic peak at ~470 °C). The last broad peak from 500 °C onwards was attributed to the decarbonation of HMCs as well as calcite, forming MgO and CaO.

Fig. 5.5 Mass loss of all samples after 28 days of 10% CO₂ curing via TGA/DSC curves

Table 5.2 Decomposition reactions and corresponding temperatures observed within RMC and dolomite samples

Phase	Decomposition reactions		
	50 – 300 °C	300 – 500 °C	> 500 °C
Brucite, Mg(OH) ₂	-	Mg(OH) ₂ → MgO + H ₂ O	-
Hydromagnesite, 4MgCO ₃ ·Mg(OH) ₂ ·4H ₂ O	4MgCO ₃ ·Mg(OH) ₂ ·4H ₂ O → 4MgCO ₃ ·Mg(OH) ₂ + 4H ₂ O	4MgCO ₃ ·Mg(OH) ₂ → 4MgCO ₃ + MgO + H ₂ O	MgCO ₃ → MgO + CO ₂
Nesquehonite, MgCO ₃ ·3H ₂ O	MgCO ₃ ·3H ₂ O → MgCO ₃ + 3H ₂ O	-	MgCO ₃ → MgO + CO ₂
Calcite, CaCO ₃	-	-	CaCO ₃ → CaO + CO ₂

Table 5.3 A summary of the mass loss values of all samples after 28 days of 10% CO₂ curing

Sample	Weight loss (wt.%)			Total (%)
	50 – 300 °C	300 – 500 °C	500 – 800 °C	
M	7.7	28.7	3.0	39.4
M75D25	8.1	24.3	8.0	40.4
M50D50	8.1	20.0	14.1	42.2
M25D75	6.9	16.6	20.8	44.3
D800	6.2	11.5	29.3	47.0

The mass loss values associated with the decomposition of all samples after 28 days of 10% CO₂ curing are listed in Table 5.3. Although the overlapping peaks of several decomposition reactions presented a challenge in identifying the exact compositions of each phase, a clear trend in the total mass loss was observed with increasing dolomite and hence, increasing calcite contents. All samples presented similar values that ranged between 6.2 and 8.1% in the temperature range of 50-300 °C. The difference in the mass losses became more obvious between 300-500 °C, during which values of 11.5-28.7% were revealed. The mass loss observed in this temperature range was mainly attributed to the decomposition of uncarbonated brucite and dehydroxylation of hydromagnesite. In line with the phase quantification results presented in Table 5.1, the control sample M, which contained the highest uncarbonated brucite content amongst all samples, revealed the highest mass loss value between 300-500 °C, as listed in Table 5.3. The mass loss values within the temperature range of 500-800 °C, mainly attributed to the decomposition of calcite and HMCs, increased with increasing carbonate contents. Sample D800, containing the highest amount of calcite, demonstrated the highest mass loss amongst all samples, which was also partially attributed to the decarbonation of HMCs (i.e. hydromagnesite and nesquehonite). These results were in agreement with the phase quantifications and carbonate contents presented in Table 5.1, highlighting the complementing role MgO

and calcite contents play in the strength development of RMC and dolomite-based samples.

5.1.1.6 Microstructure

The microstructures of all samples after 28 days of 10% CO₂ curing via scanning electron microscope are shown in Fig. 5.6. The main HMC phase observed within all formulations was hydromagnesite, along with minor formations of nesquehonite in some. The control sample M demonstrated the formation of large rosette-like hydromagnesite similar to those reported in previous studies (Braithwaite and Zedef 1996, Li, Ding et al. 2003), with a diameter of around 0.8 μm and a thickness of < 0.1 μm , as shown in Fig. 5.6(a). Hydromagnesite co-existed with unhydrated MgO and uncarbonated brucite particles within sample M. Samples M75D25, M50D50 and M25D75 revealed similar microstructures, in which the hydromagnesite crystals of various dimensions dominated the microstructure. MgO and brucite particles could also be seen within these samples, albeit at much smaller contents than sample M. An increase in the dolomite content led to the densification of the microstructure via the formation of an inter-connected carbonate network containing interlocked Mg- and Ca-based carbonates. The increased densities of samples M75D25, M50D50 and M25D75 explained their improved performance in comparison to samples M and D800 at 28 days. In addition to hydromagnesite, the formation of nesquehonite with a diameter ranging from 0.2 to 0.4 μm could be visibly observed within sample D800, which was also consistent with XRD results. These results were in line with the findings of previous studies (De Silva, Bucea et al. 2006), which also reported the key role carbonation and the morphology of carbonates play in the performance of cement-based binders.

(a)

(b)

(c)

(d)

(e)

Fig. 5.6 Microstructural images of all samples after 28 days of 10% CO₂ curing: (a) M, (b) M75D25, (c) M50D50, (d) M25D75 and (e) D800

Sample M75D25, which outperformed all others in terms of performance at 28 days, was also investigated by EDX. The results of the elemental analysis shown in Fig. 5.7(a) revealed the presence of Mg, O and C in the rosette-like cluster phases, suggesting the presence of HMCs (i.e. hydromagnesite). Investigation of the elemental spectrum at an alternate point within the same sample demonstrated the presence of Mg, Ca, O and C in Fig. 5.7(b). This observation confirmed the role calcite particles played in the formation of Mg-based carbonate phases, enabling the development of a dense carbonate network and associated strength gain.

Fig. 5.7 Elemental analysis of sample M75D25 after 28 days of 10% CO₂ curing at (a) point 1 and (b) point 2

5.1.2 Conclusion

1. The calcination temperature of dolomite determined its performance as a binder by changing its chemical composition. Calcining dolomite at 800 °C revealed a useful binder composed of MgO and calcite.

2. The main factors that determined the performance of RMC formulations were the MgO, dolomite and water contents within the initial mix design. These factors influenced the initial porosity as well as the degree of carbonation and the morphology of the final carbonate phases.

3. The MgO content influenced the amount of hydrate and carbonate phases that formed, whereas the calcite within dolomite contributed to the formation a dense carbonate network and provided nucleation sites, which improved the hydration and carbonation of MgO by providing additional surface for the continuation of these reactions.

4. Samples involving the simultaneous use of RMC and dolomite led to improved performance when compared to others, revealing 28-day strengths as high as 57 MPa, which were up to 60% higher than the control samples containing only MgO or dolomite. The mechanical properties of RMC and calcined dolomite samples were comparable, indicating that dolomite can be used as a new type of raw material for RMC source without sacrificing the mechanical performance, and the cost of RMC was greatly reduced. These strength results were in line with the decreasing porosity of these samples, which reflected the reduction in the initial pore volume due to the formation of carbonate phases.

5. The main Mg-carbonate phase observed within the samples was hydromagnesite, accompanied with small amounts of nesquehonite. The size

of the hydromagnesite crystals changed with the introduction of dolomite into RMC samples. The interlocked formations of hydromagnesite along with the nesquehonite needles led to the development of a dense carbonate network and increased the density of samples involving the simultaneous use of RMC and dolomite. These changes in sample microstructure could explain their improved performance in comparison to samples in which RMC or dolomite was used as the main binder.

5.2 Mechanical performance and carbon sequestration of RMC and calcined dolomite formulations under different curing conditions

5.2.1 Results and discussion

5.2.1.1 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 3.4, 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. 5.8.

Fig. 5.8 14-day compressive strength of concrete samples containing dolomite calcined at different temperatures under CO₂ curing

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 3.4. 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 (Itatani K, Shiobara M et al. 2002, Altiner and Yildirim 2017). Another study (Mo, Deng 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.

5.2.1.2 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. 5.9 (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.

(a)

(b)

Fig. 5.9 Isothermal calorimetry results showing the (a) heat flow (mW/g) and (b) cumulative heat (J/g) of selected samples, indicated per gram of dry binder, at 30 and 60 °C

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.

5.2.1.3 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. 5.10 (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).

Fig. 5.10 Compressive strength of all samples under different conditions, showing the (a) strength development during 14 days of CO₂ curing and (b) 14-day strengths per unit of MgO content

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, Simeon et al. 2015, Ruan and Unluer 2017, Ruan and Unluer 2017).

In addition to the initial mix design, the strength results shown in Fig. 5.10 (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. 5.9 (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. 5.11. 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.

Fig. 5.11 Microscopic images of surfaces of samples cured under 60 °C and 90% RH, 10% CO₂ containing (a) RMC and (b) D800 (magnification: x84)

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. 5.10(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.

5.2.1.4 Crystal mineral components

The major phases within selected carbonated RMC and D800 samples after 14 days of CO₂ curing are shown in Fig. 5.12. 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. 5.13, were used to normalize the phase quantification results obtained from Rietveld refinement, as described in (Scrivener, Snellings 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 5.4 and 5.5, 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.

Fig. 5.12 Major phases within selected carbonated (a) RMC and (b) D800 samples for 14 days of CO₂ curing via XRD patterns (P: Periclase; B: Brucite; H: Hydromagnesite; N: Nesquehonite; C: Calcite)

(a)

(b)

Fig. 5.13 Mass loss of selected (a) RMC and (b) D800 samples via TGA curves after 14 days of CO₂ curing

Table 5.4 Percentage quantities of the major phases within selected samples after 14 days of curing, obtained via Rietveld refinement (i.e. before normalization)

Sample	MgO (wt.%)	Brucite (wt.%)	Nesquehonite (wt.%)	Hydromagnesite (wt.%)	Calcite (wt.%)
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 5.5 Quantities of the major phases shown in Table 5.4, normalized to ignited binder mass (in g/100g paste)

Sample	MgO (g)	Brucite (g)	Nesquehonite (g)	Hydromagnesite (g)	Calcite (g)
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

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 3.4. 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.

5.2.1.5 Microstructure

The formation and morphology of phases within carbonated RMC and D800 samples that revealed the highest and lowest strengths were illustrated with microstructural images via scanning electron microscope shown in Fig. 5.14. 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.

Fig. 5.14 Microstructural images of selected RMC and D800 samples cured for 14 days: (a) M-R50T30C10, (b) M-R90T60C10, (c) D-R50T30C10 and (d) D-R90T30C10; and EDX results of (e) point 1 and (f) point 2 via scanning electron microscope

5.2.2 Conclusion

1. 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.

2. 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.

3. 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.

4. The optimum curing conditions were different for each binder system and must be customized accordingly to facilitate hydration and carbonation and achieve maximum performance within each formulation.

Chapter 6 DEVELOPMENT OF RMC-BASED STRAIN-HARDENING COMPOSITES WITH THE ABILITY TO UNDERGO SELF-HEALING

Although continuous research on RMC formulations has achieved significant improvements in terms of mechanical performance, RMC-based concrete is still considered as a brittle material, which could highly benefit from the use of reinforcement in the development of structural members. Nevertheless, the relatively low pH (i.e. ~ 10) of carbonated RMC formulations presents a challenge in the use of steel reinforcement (Pu and Unluer 2016), which can face a risk of corrosion due to the loss of the passivated surface at such relatively low alkalinities, thereby potentially creating structural safety issues. To increase the application spectrum of RMC within the construction industry, it is curial to develop alternative methods that will enhance the ductility of RMC-based formulations.

This chapter presents the results of an investigation focusing on the strain hardening and self-healing behaviors of RMC formulations involving the introduction of polyvinyl alcohol (PVA) fibers under different healing conditions. The first part of this study focused on the development of a new strain-hardening composite (SHC) involving carbonated RMC and pulverized fly ash (PFA) as the main binder. Rheological properties of the developed composites were investigated by varying FA and water contents to achieve a desirable fiber dispersion. A suitable mix design, in which PVA fibers were introduced to provide tensile ductility, was determined. The effect of key parameters such as w/b ratio and curing age on the mechanical properties of carbonated RMC-SHC was evaluated. The mix designs used in this study are shown in Tables 3.11 and 3.12.

The second part of this study investigated the feasibility of RMC-based SHC formulations to engage in autogenous healing under a variety of conditions involving the use of CO₂, water and bacteria-based healing. The effects of the

conditioning regimes on the healing efficiency were reported via the use of surface crack width measurement, resonance frequency recovery, X-ray micro-computed tomography (μ -CT), and uniaxial tensile tests. The formation of self-healing products were characterized using SEM and EDX. The compositions and other properties of the healing products were further explored with XRD and pH measurements. The mix designs used in this study are shown in Tables 3.14 and 3.15.

6.1 Strain-hardening behavior of RMC formulations

6.1.1 Results and discussion

6.1.1.1 Rheological properties

Fig. 6.1 illustrates the typical relationship between the shear resistance τ (Pa) and shear rate N (/s) of a fresh RMC mixture at different elapsed times. The curves show that the fresh mixtures were Bingham liquids, in which the shear force exceeded the initial mixture resistance to initiate rotation, after which the shear resistance increased linearly with the rotation speed N (/s), showing no shear thinning or thickening effect. The relationship between τ and N of Bingham liquids is quantitatively described by Equation 6.1, where g (Pa), the intercept on the y-axis, is the yield stress needed to break the network of interactions between particles and initiate rotation; and h (Pa · s), the slope of the curve, is the plastic viscosity (Ferraris, Martys et al. 2014). For any given fresh mixture at a designated time, g and h are constants that represent the rheological properties of that mixture.

$$\tau = g + N \cdot h \quad (6.1)$$

Fig. 6.1 τ - N curve of sample FA60-0.53 at 6, 12 and 18 minutes, showing (a) overall test results and (b) section selected in (a)

In regular cement-based fresh mixes, shear resistance, which varies with shear rate ($\dot{\gamma}$) and solid volume fraction (V_s), depends on several types of particle interactions (i.e. Van der Waals forces, direct contact forces between particles and hydrodynamic forces, for which the friction between fluid layers increases with velocity) (Roussel, Lemaître et al. 2010). At relatively low shear rates (i.e. whose threshold depends on the w/b ratio (Lootens, Van Damme et al. 2003, Phan, Chaouche et al. 2006)), the yield stress (σ_y) is mainly determined by Van der Waals or direct contact forces. Previous studies on the yield stress of C₃S pastes (Mansoutre, Colombet et al. 1999) showed that a critical V_s existed at 0.38, beyond which the solid particles became so compacted that the dominant particle interaction shifted from Van der Waals to direct contact forces. As C₃S and RMC have a comparable particle size distribution (Pu and Unluer 2016), and they both conform to Bingham model, the information on C₃S was used to evaluate the behavior of RMC-based samples. It must be noted that the yield stress can also be related to the surface chemistry of particles, which was not differentiated here. Most of the mix designs presented in this study, except for FA0-0.58 ($V_s = 0.35$) and FA30-0.58 ($V_s = 0.37$), had V_s values that were larger than 0.38, indicating the dominance of direct contact forces. At relatively high shear rates, the yield stress is majorly determined by hydrodynamic forces, while the effects of Van der Waals and direct contact forces still exist.

The measured values of the yield stress (σ_y) and plastic viscosity (η_p) of all samples at different elapsed times are provided in Table 6.1. For some mixes, the values of σ_y and η_p at 12 and 18 minutes were not listed due to the loss of contact between the top plate and the fresh mixture, resulting in the underestimation of shear resistance. A generally increasing trend in σ_y and η_p was observed with elapsed time. This was possibly associated with the precipitation of brucite (Mg(OH)₂) on the surface of RMC particles (Rocha, Mansur et al. 2004), which increased the direct contact between particles by enlarging the solid particle size and leading to additional drag between fluid layers.

Table 6.1 Results of rheological test in this study

Sample	Elapsed time = 6 min		Elapsed time = 12 min		Elapsed time = 18 min	
	g (Pa)	h (Pa·s)	g (Pa)	h (Pa·s)	g (Pa)	h (Pa·s)
FA0-0.58	60.6	1.15	-	-	-	-
FA30-0.47	153.1	5.55	-	-	-	-
FA30-0.53	172.8	3.66	183.3	4.79	-	-
FA30-0.58	48.0	2.59	76.0	3.29	94.8	4.66
FA60-0.47	26.2	2.24	40.3	2.66	54.8	3.14
FA60-0.53	6.1	1.13	11.0	1.93	31.0	3.41
FA60-0.58	2.1	0.43	1.6	0.44	5.5	1.17

* “-“ indicates g and h were underestimated due to the loss of contact between the top plate and the fresh mixture

The effects of water and FA contents on the rheological properties of RMC samples are shown in Fig. 6.2, where a declining trend in g and h was observed with increasing water content at both FA/b ratios of 0.53 and 0.58. The reduction in plastic viscosity and yield stress with increasing w/b ratios could be attributed to the higher liquid content that decreased direct contact amongst particles. Regarding the effect of FA content, the trend in g and h values at different FA contents ranging between 0% and 60% was shown at a w/b of 0.58. An increase in the FA content from 0 to 30% (i.e. $V_s < 0.38$, Van der Waals forces dominate) led to an increase in plastic viscosity, while it did not have a profound effect on the yield stress. This increase in the plastic viscosity could be due to the enhanced Van der Waals forces via the reduction of the distance between particles as V_s increased from 0.35 to 0.37. The constant yield stress of samples FA0-0.58 and FA30-0.58 could be associated with the loose compaction of particles within these two mixes, thereby limiting the effect of particle shape on Van der Waals forces. A further increase in the FA content from 30% to 60% (i.e. $V_s > 0.38$, direct contact force dominates) resulted in the decline of both g and h at all w/b ratios. Although an increase in the solid volume fraction with an increase in the FA content could be expected due to the lower density of FA than RMC (2400 vs. 3230 kg/m³), the reduction of the yield stress and plastic viscosity with

increasing FA content could be attributed to the spherical geometry of FA particles, which reduced the contact force between particles.

Fig. 6.2 Effects of the water and FA contents on the (a) plastic viscosity and (b) yield stress of RMC samples

6.1.1.2 Mechanical performance

Based on the rheological results mentioned in Section 6.1.1.1, samples containing 30% FA (i.e. FA/b = 0.3) with different w/b ratios (0.41-0.53) and curing ages (7 and 28 days) were prepared for compression and uniaxial tensile tests. The obtained results are presented in Table 6.2. The tensile stress recorded at the occurrence of the first crack is referred to as the “first cracking strength”, whereas the tensile stress and tensile strain approaching specimen failure are referred to as the “ultimate tensile strength” and “tensile strain capacity”, respectively. In addition to the first cracking strength, ultimate tensile strength, and tensile strain capacity, crack spacing and average crack width of each sample are also provided in Table 6.2.

Table 6.2 Results of mechanical test in this study

Sample	Age (days)	Compressive strength (MPa)	Results of uniaxial tensile test				
			First cracking strength (MPa)	Ultimate tensile strength (MPa)	Tensile strain capacity (%)	Crack spacin g* (mm)	Average crack width (μ m)
RMC- 0.53	7	4.60	1.09	1.32	1.40	12.80	146.80
		± 0.07	± 0.11	± 0.09	± 0.66	± 3.50	± 22.90
RMC- 0.47	7	16.27	1.60	2.89	2.13	2.66	49.74
		± 0.47	± 0.13	± 0.26	± 1.02	± 1.10	± 12.88
RMC- 0.41	7	18.97	2.19	2.61	2.64	1.45	47.21
		± 0.48	± 0.48	± 0.48	± 1.22	± 0.14	± 15.08
	28	-	2.38 ± 0.24	3.67 ± 0.35	2.70 ± 0.96	1.74 ± 0.27	63.77 ± 10.38

*Crack spacing (mm) = Gauged length extension/crack number; a smaller crack spacing is usually associated with a higher degree of strain-hardening.

The relationship between the tensile stress and strain within each mix are shown in Fig. 6.3. Distinct elastic and strain-hardening stages were observed within each sample. In the elastic stage, the tensile stress developed linearly with the strain. The continuous increase in the load led to the introduction of the first crack, which marked the beginning of the strain-hardening stage. During the strain-hardening stage, tensile stress increased slowly with the strain, accompanied with the progressive generation of multiple fine cracks that indicated ductility. Towards the end of strain-hardening, tensile stress started to drop dramatically due to the deterioration of fiber bridging followed by damage localization with increasing load. At this point, the load was released immediately after specimen failure, leading to the shrinking of a majority of the cracks due to the spring effect of fiber-bridging. Fig. 6.4 shows the typical crack distribution on a failed specimen after unloading, highlighting the occurrence of multiple cracking in RMC samples. The typical fracture surface can be seen in Fig. 6.5(a), where the layout of fibers at the location

of the crack at failure is revealed. The pulled-out fiber and the leftover fiber tunnel at a fracture point are shown in Fig. 6.5(b) and (c), respectively. As can be seen from these images, the fiber surface was smooth with a very small amount of matrix debris attached on it, showing that a majority of the fibers were pulled out instead of ruptured. This suggests the fiber strength was not fully utilized in the developed formulations and the limiting phase was the fiber-matrix interface, which may be further strengthened.

Fig. 6.3 Tensile stress vs. strain curves of samples (a) RMC-0.53-7d, (b) RMC-0.47-7d, (c) RMC-0.41-7d and (d) RMC-0.41-28d

Fig. 6.4 Crack pattern of a typical sample (RMC-0.41 at 7 days of CO₂ curing)

(a)

(b)

(c)

Fig. 6.5 Illustration of a typical failed specimen (RMC-0.41 at 7 days of CO₂ curing), showing the (a) fracture surface with several pulled fibers, (b) FESEM image of a pulled-out fiber and (c) FESEM image of a left-over tunnel from the pulled fiber

(i) Influence of w/b ratio on the mechanical properties of RMC-SHC samples

The results obtained after the mechanical testing of samples RMC-0.53, RMC-0.47 and RMC-0.41 are listed in Table 6.2. The influence of w/b content on the performance of each sample was observed both in terms of compressive and tensile strengths. As could also be seen in Fig. 6.3, the mechanical properties were enhanced when the w/b reduced from 0.53 to 0.47, where a less pronounced change was observed as the w/b further reduced to 0.41.

The initial reduction in the w/b from 0.53 to 0.47 led to a compressive strength that was almost four times higher (4.6 vs. 16.3 MPa). This was accompanied with a 50% increase in the first tensile crack strength, which mainly depended on the matrix performance. This improved performance could be associated with the increased diffusion rate of CO₂ in a less saturated pore system, as well as the higher initial density provided by the lower water content within sample RMC-0.47. The increased diffusion of CO₂ could translate into a higher degree of carbonation and hence the formation of strength providing HMCs (Unluer and Al-Tabbaa 2014). The other tensile properties, such as the ultimate tensile strength and ductility, which were mainly determined by the fiber-bridging, were also improved under lower water contents. The ultimate tensile strength was more than doubled, while the ductility was increased by about 50%. The reduction in crack spacing indicated that strain-hardening became more robust as the w/b ratio decreased. The enhanced fiber bridging, which was clearly indicated by the reduced crack width, could also be attributed to the higher degree of carbonation and denser microstructure at the fiber/matrix interface (Kanda and Li 1998, Li, Qiu et al. 2017). When compared to RMC-0.53, the enhanced fiber-bridging of RMC-0.47 also led to a higher complementary energy J'_b , resulting in a more saturated multiple cracking. The reduced crack width would be especially important for any potential crack healing (Yang, Lepech et al. 2009).

A further decrease in the w/b ratio from 0.47 to 0.41 (i.e. at 7 days) led to improved mechanical performance, albeit at a lower rate than previously

observed. When compared to the increase in performance when the w/b changed from 0.53 to 0.47, the lower rate of increase observed in the transition of the w/b from 0.47 to 0.41 could be explained by the limited hydration of RMC due to the lower availability of water, which could have also hindered the formation of HMCs in the longer term. On the other hand, as the diffusion of CO₂ is faster in drier environments, the relatively low w/b of 0.41 could have provided the right medium for increased carbonation, which can explain the higher compressive strength results of sample RMC-0.41 (Unluer and Al-Tabbaa 2014). Another factor that may have contributed to the relatively higher strength results of this sample was its reduced porosity within the interfacial zone of fiber-matrix under the low water content, thereby resulting in a denser structure than samples RMC-0.47 and RMC-0.53. The reduction in crack spacing and average crack width were also an indicator of improved strain-hardening and fiber bridging.

(ii) Influence of curing age on the mechanical properties of RMC-SHC samples

While a robust strain-hardening and ultra-high ductility were achieved in RMC-SHC samples, their mechanical properties were still not at the same level as typical PC-based SHC, whose ultimate tensile strength and ductility can easily reach 5 MPa and 3-5%, respectively (Yang, Yang et al. 2007). Accordingly, samples with the highest ductility (RMC-0.41) were chosen to be exposed to additional CO₂ curing for up to 28 days to explore the full potential of RMC-SHC samples in terms of tensile strength enhancement. A comparison of samples RMC-0.41-7d and RMC-0.41-28d revealed an increase in the ultimate tensile strength by ~40%, which could be attributed to the continued formation of carbonate phases that strengthened the fiber/matrix interface over the 28-day curing period (Unluer and Al-Tabbaa 2014). On the other hand, there were no notable changes in the tensile ductility, crack spacing and crack width. These results indicated the feasibility of enhancing the ultimate tensile strength of RMC-SHC formulations via the effective use of additional CO₂ curing, during which their strain-hardening

robustness was not compromised.

6.1.1.3 Carbon sequestration

The amount of CO₂ sequestered during the curing process was quantified via TGA/DSC, a representative curve for which is shown in Fig. 6.6. The mass loss < 100 °C due to the loss of hygroscopic water was followed by two distinct endothermic peaks. The first peak at around 320 °C corresponded to the removal of water of crystallization in Mg-carbonates that formed during carbonation curing and the decomposition of uncarbonated hydrates (Mg(OH)₂) into MgO. The second peak at around 460 °C corresponded to the decarbonation of carbonate phases, leaving MgO at the end of the analysis. The quantification of the mass loss at > 460 °C, which was associated with the loss of CO₂ from the carbonated RMC system, revealed an average carbonation degree of around 10%. A similar outcome can be expected under ambient carbonation conditions, albeit at a much slower rate due to the low concentration of CO₂ in the atmosphere (0.04%). These results indicate that the sequestration of CO₂ in the form of stable carbonates within the prepared formulations can not only provide a safe storage under accelerated CO₂ curing, but also contribute to the development of a new type of strain-hardening composite that does not necessitate the use of any PC.

Fig. 6.6 Carbon sequestration of the RMC-SHC sample (RMC-0.53) through TGA/DSC curves

6.1.2 Conclusion

1. The obtained results revealed the ideal binder composition and w/b ratios that led to a relatively high plastic viscosity and sufficient flowability for desirable fiber dispersion.
2. The use of carbonation curing enhanced the strength development of RMC-SHC by improving the fiber-matrix interface bond, but not ductility. Lower water contents led to increased tensile strength and ductility, which was attributed to the strengthening of the bond between the fibers and the matrix. The prepared RMC-SHC samples, which presented a considerable CO₂ sequestration capability during the curing process, achieved an ultimate tensile strength and ductility of up to 3.7 MPa and 3.3%, respectively.
3. The RMC-FA formulations developed in this study, with a potentially lower environmental impact than corresponding PC-based mixes due to their ability to gain strength via carbonation, were considered as a promising candidate for strain-hardening composites that could be used in various building applications.

6.2 Water and CO₂-based self-healing behavior of RMC formulations

6.2.1 Results and discussion

6.2.1.1 Surface crack width

The reduction of crack width serves as an indicator of self-sealing degree. Fig. 6.7 plots the crack width of pre-cracked RMC-based SHC specimens before and after environmental exposures, where the x-axis is the original crack width and the y-axis is the corresponding crack width after conditioning. The 45-degree dashed line thus indicates no reduction of crack width after conditioning, while the distance of each data point to the 45-degree line represents the reduction of crack width due to self-healing. For specimens

subjected to air conditioning, crack widths remain the same, as all data points are on the 45-degree line (Fig. 6.7(a)) and no apparent sealing of cracks can be observed visually under optical microscope (Fig. 6.8(a)). Specimens subjected to water/air conditioning show moderate reduction of crack width (Fig. 6.7(b)), where some cracks below 30 μm show the potential to be completely sealed (Fig. 6.8(b)). Conditioning regimes involving a higher concentration of CO_2 , i.e. water/ CO_2 or CO_2 , resulted in a significant reduction in crack width and almost all the cracks were completely sealed. However, in some cases, the healing only took place on the surface and cracks at inner sections remained unhealed (Fig. 6.8(c)). This may be attributed to that elevated CO_2 concentrations accelerated the formation and growth of carbonate phases on the surface, and the formed crystals prevented a further penetration of CO_2 into cracks, leading to a low extent of carbonation at the inner sections of the cracks. The slight difference between the water/ CO_2 conditioning and the CO_2 conditioning, where a few cracks were not fully sealed in the latter scenario, highlighted the important role of water, which facilitated the continuation of hydration and carbonation within the crack in self-healing.

Fig. 6.7 Crack widths of RMC-based SHC specimens before and after (a) air, (b) water/air, (c) water/CO₂, and (d) CO₂ conditioning; for each data point, the distance to the 45-degree dashed line indicates the crack width reduction on the surface

(a)

(b)

(c)

Fig. 6.8 (a) No apparent crack sealing of specimens subjected to air conditioning; (b) complete crack sealing of specimens subjected to water/air conditioning; and (c) crack sealing on the surface of specimens subjected to water/CO₂ and CO₂ conditionings

6.2.1.2 Resonant frequency

Monitoring the resonant frequency throughout the conditioning period serves as a non-destructive method to understand the healing-induced mechanical recovery, especially the recovery rate. The changes of RF under different regimes are shown in Fig. 6.9 as a function of the number of conditioning cycles. As can be seen, the RF of pre-strained specimens was remarkably lower than that of the control specimens (without pre-straining) prior to conditioning due to the formation of multiple cracks that reduced the stiffness of the specimens. It is also noteworthy that the RF of control specimens remained unchanged with prolonged conditioning for all four conditioning regimes, indicating a limited carbonation capacity of the control specimens under the four conditioning regimes involved, which could be related with a densified microstructure formed on the surface, inhibiting a further penetration of CO₂ into mixes. As shown in Fig. 6.9(a), the RF of pre-strained specimens subjected to air conditioning slightly recovered during the first two cycles, resulting from the carbonation of the remaining brucite induced by a low amount of CO₂ in the air (i.e. 0.04%). However, even after 20 days of air conditioning, the RF of pre-strained specimens was still significantly lower than that of the control group. As shown in Fig. 6.9(b), the specimens under the water/air regime presented a significant RF recovery, and it increased almost linearly with the growth of healing cycles. Furthermore, the effect of pre-strain level on the RF recovery rate and degree is pronounced. The RF recovery of WA-5 (0.5% pre-strain) was significantly faster than that of WA-10 (1.0% pre-strain). The RF of WA-5 returned to the same level (i.e. complete recovery) as that of control (WA-0) after 4 healing cycles and exceeded the control afterwards, whereas the RF of WA-10 reached the same level as the control after 10 healing cycles. The reduced RF recovery with increasing pre-strain level was also reported in PC-based SHC healed under water/air regime (Yang, Lepech et al. 2009, Yang, Yang et al. 2011), which is attributed to a slightly larger width and a much larger number of cracks at a higher pre-strain level (Table 3.14). As shown in Fig. 6.9(c), the specimens under the water/CO₂ regime (WC) also showed a significant RF

recovery to the same level as the control. However, it seemed such recovery was independent from the pre-strain level, as both WC-5 and WC-10 exhibited a similar RF recovery rate and degree. As shown in Fig. 6.9(d), the specimens under CO₂ regime (C) only demonstrated a slight RF recovery for the first 4 cycles; after which the RF became stable, which is probably due to the absence of water as water is the medium for both hydration and carbonation, leading to a smaller amount of HMCs formation in mixes when water is not adequate (Vandeperre and Al-Tabbaa 2007, Unluer and Al-Tabbaa 2014).

Fig. 6.9 Resonant frequency recovery of RMC-based SHC samples subjected to (a) air, (b) water/air, (c) water/CO₂, and (d) CO₂ conditioning

In summary, WA-5 exhibited the best RF recovery, followed by WC-5 ($\approx$ WC-10), WA-10, and A-5 ($\approx$ C-5), i.e. $WA-5 > WC-5 \approx WC-10 > WA-10 > A-5 \approx C-5$, indicating water immersion is essential to engage significant RF recovery. At a relatively lower pre-strain level, WA conditioning regime revealed the best RF recovery and it even outperformed the control samples in terms of RF recovery, however, its recovery rate and degree was sensitive to the pre-strain level. A different scenario was seen in WC conditioning regime, which was less dependent on the pre-strain level.

6.2.1.3 Tensile behavior

Fig. 6.10 shows the typical tensile stress-strain curves (pre-straining before conditioning and re-loading after conditioning) of RMC-based SHC together with that of the control specimen after conditioning. After the pre-straining and unloading, residual strain due to crack opening was recorded. Table 6.3 summarizes the post-conditioning tensile properties of samples and Fig. 6.11 compares recovery of mechanical properties subjected to different conditioning regimes by normalizing the properties of corresponding control groups (i.e. A-0, WA-0, WC-0 and C-0).

The tensile elastic stiffness, in contrast with RF, is a direct measure to determine the mechanical recovery. As shown in Fig. 6.11(a), the elastic stiffness of the A-5 specimens was only 11% of its control, while the other groups demonstrated stiffness ratios significantly greater than that of A-5, indicating that there was a stiffness recovery in the presence of water and/or CO₂. As for the effect of conditioning regimes and pre-strain levels, the recovery of elastic stiffness revealed a similar trend to that of RF, where WA-5 revealed the highest stiffness ratio and was the only group that recovered to more than 100% of its control, followed by WC-5/10, WA-10, and C-5. As expected, the pronounced effect of pre-strain level was only observed in samples subjected to water/air conditioning instead of water/CO₂ conditioning.

(a)

(b)

(c)

(d)

(e)

(f)

Fig. 6.10 Pre-loading and reloading uniaxial tensile stress-strain curves of (a) A-5, (b) WA-5, (c) WA-10, (d) WC-5, (e) WC-10, and (f) C-5 specimens

Table 6.3 Post-conditioning tensile properties of RMC-based SHC

Group	Elastic stiffness (GPa)	First cracking strength [#] (MPa)	Ultimate tensile strength (MPa)	Reloading strain capacity (%)	Total strain capacity [^] (%)	Crack spacing after failure (mm)
A-0*	8.91±3.76	2.76±0.60	3.08±0.34	-	1.69±0.40	7.3±5.5
A-5	1.01±0.37	2.58±0.24	3.01±0.13	1.33±0.76	1.47±0.36	5.8±4.2
WA-0*	7.85±3.16	2.46±0.26	3.02±0.15	-	1.33±0.37	6.9±5.8
WA-5	8.26±1.52	2.36±0.48	3.71±0.27	1.92±0.95	2.30±0.49	3.2±1.7
WA-10	4.13±1.43	1.94±0.33	3.03±0.77	1.14±1.12	1.66±0.58	4.3±2.7
WC-0*	9.13±5.92	2.43±0.38	2.96±0.45	-	1.11±0.26	9.7±6.1
WC-5	6.78±3.13	2.52±0.39	3.41±0.50	1.41±0.77	1.60±0.44	4.2±3.4
WC-10	6.02±1.50	2.38±0.45	3.41±0.20	1.41±0.99	1.84±0.50	7.6±4.0
C-0*	8.39±1.52	1.71±0.67	2.56±0.44	-	1.89±0.76	11.3±4.4
C-5	3.82±1.11	1.52±0.14	2.85±0.24	1.88±0.93	2.01±0.29	9.0±8.9

* included as the control group cured under the same conditioning regime.

[#] for group A-5, WA-5, WA-10, WC-5, WC-10 and C-5, the value was taken as the tensile stress at the end of elastic stage.

[^] for group A-5, WA-5, WA-10, WC-5, WC-10 and C-5, the value equals to the residual strain from pre-loading plus the strain due to re-loading.

Fig. 6.11 (a) Elastic stiffness ratio, (b) ultimate tensile strength ratio, and (c) strain capacity ratio of RMC-based SHCs subjected to different conditioning regimes normalized by the properties of corresponding control groups (i.e. A-0, WA-0, WC-0 and C-0)

The ultimate tensile strength is a direct measure of healing-induced fiber-bridging enhancement (Yang, Wang et al. 2008, Qiu and Yang 2016). Fig. 6.11(b) shows the ultimate tensile strength of each group in comparison to their corresponding control groups. As expected, there was no tensile strength boost in A-5 subjected to air conditioning. After water/air conditioning, WA-5 demonstrated a great strength improvement, however, there was no strength improvement in WA-10, indicated by a larger crack number and crack width (Table 6.3). Regarding the water/CO₂ conditioning, it was still

independent from pre-strain level, as both WC-5 and WC-10 achieved a great mechanical improvement. For some samples with better mechanical properties, the cracking localization eventually occurred at one of the new cracks generated during reloading, instead of the old cracks that previously formed during pre-loading (Fig. 6.12). The tensile strength improvement, or essentially the fiber-bridging strength boost, could be attributed to a stronger fiber/matrix interfacial bond as a quantity of healing products forming at the cracks between the fibers and the matrix (Qiu and Yang 2017). C-5 subjected to CO₂ conditioning revealed almost no strength improvement, confirming the necessity of water immersion to engage the increase of strength.

(a)

(b)

Fig. 6.12 Residual cracks on a healed specimen (WC-5) after reloading; the fine white strips are the cracks generated during pre-loading. Cracking localization, as indicated by the semi-transparent red bands, occurred at new cracks that were generated during reloading (unit on the ruler: centimeter)

Fig. 6.11(c) shows tensile strain capacity (of both reloading and total) of each group in comparison to their corresponding control group. The significantly increased strain capacity ($>100\%$), especially that under the reloading test, were only observed in the groups with a significant fiber-bridging improvement, such as WA-5, WC-5/10. After reloading, these groups presented a smaller crack spacing compared to their controls (Table 6.3). The strong correlation between ultimate strength and strain capacity can be attributed to the additional supplementary energy to induce new cracks in the matrix provided by the enhanced fiber-bridging strength (Li, Qiu et al. 2017), and such correlation was especially stronger in RMC-based SHC as compared to its PC-based counterpart, as the strength and toughness of RMC-based matrix failed to increase with the continuous conditioning possibly, which is implied from the RF results (Fig. 6.9).

6.2.1.4 Microstructure

After reloading, both the near-surface regions and the interior regions of the healed cracks were characterized with FESEM and EDX. Typical microstructure and elementary composition of the samples conditioned under water/air (WA) and water/ CO_2 (WC) cycles are shown in Fig. 6.13 and 6.14, respectively. It can be seen that under both WA and WC conditioning, a significant amount of healing products formed inside the crack, the original profile of which is highlighted with the dashed lines. Under WA conditioning, the healing products were observed both on the surface (Fig. 6.13(a)) and at the inner sections (Fig. 6.14(b)) of the crack. However, under WC conditioning, a high density of packed healing products was only present near the surface regions (Fig. 6.14(a)) and nearly no healing products were identified in the interior parts of the crack (Fig. 6.14(b)). The EDX mapping (Fig. 6.13(b) and Fig. 6.14(a)) shows that the healing products inside the cracks were rich only in Mg and C, while the surrounding matrix also consists of Si due to the presence of pulverized fly ash (PFA) in the mix, and the healing products were recognized as HMCs, resulting from the continued hydration and carbonation of RMC.

Fig. 6.13 Distribution of element C, Mg and Si (colored region and black region indicate the presence or absence of the element) via elemental mapping within of healing products formed under water/air conditioning (WA): (a) the microstructure of near surface region of the healed crack; (b) the microstructure and EDX mapping (the entire image b1) of interior region of the healed cracked. The dashed lines show the original crack width

(a)

(b)

Fig. 6.14 Distribution of the element C, O, Mg and Si (colored region and black region indicate the presence or absence of the element) within formed healing products under water/ CO₂ conditioning (WC): (a) the microstructure and EDX mapping of the near surface region of the healed crack. The dashed lines show the crack width. (b) no healing products were identified in the interior part of the crack

Despite the similar elementary composition, the healing products of WA and WC also demonstrate distinct morphologies. The WA healing product (both Fig. 6.13(a) and (b)) is made of layers of thin flake and resembles the morphology of hydromagnesite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) or dypingite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$), which usually show rosette-like structures formed by layers of flakes (Dung and Unluer 2017, Ruan and Unluer 2017). The healing products of the group WC (Fig. 6.14(a)), however, demonstrates a needle-like or rod-like morphology, which apparently resembles that of nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) (Unluer and Al-Tabbaa 2014), which could be attributed to the ample supply of CO_2 under WC condition, favoring the formation of nesquehonite with a higher C:Mg molar ratio of 1:1, whereas hydromagnesite and dypingite with a lower C:Mg molar ratio (i.e. C:Mg=4:5) are formed in samples subjected to the WA conditioning.

6.2.2 Discussion

The healing performances under the four conditioning cycles, i.e. A, WA, WC, and C, were qualitatively assessed and compared in Table 6.4, where all the assessments in the current study are included. The air conditioning achieved almost no healing and elevated CO_2 with water spray only led to a crack sealing on the surface of the crack with almost no mechanical recovery, indicating the necessity of water immersion, acting as a medium for both hydration and carbonation process of RMC in autogenous healing (Russell, Basheer et al. 2001, Vandeperre and Al-Tabbaa 2007). While both the water/air and water/ CO_2 cycles were capable of achieving a significant crack sealing and mechanical recovery, some differences were also noticed between these two conditioning regimes in terms of the pre-strain levels of samples. The healing under WC conditioning regime was less sensitive to the pre-strain level as both WC-5 and WC-10 achieved a significant and comparable healing, whereas the healing under WA regime strongly depended on the pre-strain levels, as WA-5 achieved a larger recovery rate than WC-5/10 when the healing of WA-10 was limited. Based on the microstructural observation (optical microscopy, FE-SEM, and EDX), Fig.

6.15 illustrates schematically the crack healing of WA-5/10 and WC-5/10 specimens.

Table 6.4 Qualitative assessment of autogenous healing subjected to different conditioning regimes

Conditioning	Crack width reduction	Stiffness recovery	Tensile strength/strain capacity enhancement
Air	None	None	None
Water /Air	Medium	Excellent but sensitive to pre-strain level	Excellent but sensitive to pre-strain level
Water / CO₂	Excellent	Good and robust	Good and robust
CO₂	Good	Limited	None

In terms of WA-5 (Fig. 6.15(a)), water and CO₂ in the ambient air were more accessible into the inner sections of the crack and the rosette/flake-like healing products (i.e. hydromagnesite/dypingite) were capable of filling the entire crack from the surface to the interior regions (Fig. 6.15(a) and (b)), leading to a more robust mechanical recovery. WA-10 (Fig. 6.15(b)) represents the healing of relatively larger cracks width under water/air cycles. The inner sections of the cracks were still healed by the similar healing products, however, the formed phases failed to re-bridge the full crack width, which left a considerable length of the fiber uncovered with the healing products, resulting in a limited recovery of mechanical properties. With regard to WC-5 (Fig. 6.15(c)) and WC-10 (Fig. 6.15(d)), under a high CO₂ concentration, needle/rod-like healing products (i.e. nesquehonite) grew and densely compacted the near-surface regions of the cracks within a short period of time, even in samples with a relatively large crack width (Fig. 6.14(a)), suggesting the formation of nesquehonite favors the autogenous healing of samples with larger crack widths. However, these healing products

created barriers for further water and CO₂ penetration into the interior part of the cracks, leaving the inner sections of the cracks unhealed.

Fig. 6.15 Illustration of crack healing of (a) WA-5, (b) WA-10, (c) WC-5, and (d) WC-10

6.2.3 Conclusion

1. Autogenous healing of RMC-based SHCs was feasible under proper environmental conditionings without any external intervention. Both a complete crack sealing and significant mechanical recovery/improvement could be realized through autogenous healing.

2. The presence of water was necessary to enable autogenous healing and favored a mechanical recovery of samples. Elevated CO₂ concentrations led

to the formation of needle/rod-like healing products (i.e. nesquehonite) which was capable of sealing cracks with large widths.

3. Healing under the WC conditioning regime was more robust and less sensitive to the pre-strain levels. However, ample supply of CO₂ resulted in a fast sealing of crack on the near surface region, creating barriers for the access of further water and CO₂ into the inner sections of the cracks, leaving the interior regions of the cracks unhealed.

4. Pre-cracked RMC-based SHC samples subjected to water/air conditioning presented a high crack healing efficiency and mechanical recovery, which was even better than the control group. The entire crack from the surface to the interior regions was filled with a high density of rosette/flake-like healing products (i.e. hydromagnesite/dypingite), leading to a remarkably mechanical recovery. However, the healing under WA condition regime strongly depended on the pre-strain levels.

6.3 Bacteria-based self-healing behavior of RMC formulations

6.3.1 Results and discussion

6.3.1.1 Surface crack width

The change in the crack widths of all samples before and after conditioning was recorded and compared to assess the effectiveness of different healing regimes. Fig. 6.16 shows the crack widths of cracked RMC-based blends under various healing conditions, where the x- and y-axis represent the original crack width and corresponding crack width after conditioning, respectively. A 45-degree dashed line representing zero-healing was plotted in all figures. The vertical distance to the 45-degree dashed line was an indication of the crack width reduction as a result of the healing process. RMC-based blends subjected to A/A condition revealed almost no change in

their crack widths (i.e. all data points were located on the 45-degree dashed line) (Fig. 6.16(a)). This lack of change was also shown by optical microscopy in Fig. 6.17(a), where the crack width remained the same even after 10 cycles of air conditioning. A slight decrease in the crack openings under W/A condition was observed, during which some cracks $< 20 \mu\text{m}$ were even totally healed after 10 cycles (Fig. 6.16(b)). However, a majority of the large cracks ($> 100 \mu\text{m}$) remained unhealed under this condition (Fig. 6.17(b)). A similar finding was reported in PC-based blends that were subjected to water conditioning, in which small crack widths ($< 30 \mu\text{m}$) presented a higher potential to be fully healed when compared with larger crack openings (Qiu, Tan et al. 2016).

Fig. 6.16 Crack widths of RMC-based blends after 10 healing cycles under (a) A/A, (b) W/A, (c) B-1U/A and (d) B-2U/A conditions

Fig. 6.17 RMC-based blends before and after 10 healing cycles under (a) A/A, (b) W/A, (c) B-1U/A and (d) B-2U/A conditions

Introduction of bacteria-urea solution in the healing of RMC-based blends led to a significant reduction in the crack opening of all samples, regardless of the urea concentration, as shown in Fig. 6.16(c) and (d). Nearly all the cracks, including those with large openings ($\geq 200 \mu\text{m}$), were completely healed after 10 cycles under these conditions. This crack closure was associated by the growth of crystal phases that filled in and sealed the cracks (Fig. 6.17(c) and (d)). These findings highlighted the importance of water in facilitating the continuation of hydration and carbonation and improving the extent of autogenous healing, which was also reported in PC-based blends (Yang, Lepech et al. 2009). When compared to A/A and W/A conditions, the bacteria selected in this study, *Bacillus* species, enabled the complete healing of the cracks in RMC-based blends within a short time period. This was particularly critical for the healing of large cracks, which was attributed to the formation of a large quantity of precipitates in the presence of the bacteria. These results were in line with the findings of a previous study (Qiu, Ruan et al. 2018), where the difficulty for healing large cracks (e.g. 50-100 μm) under water conditioning was reported. This was alleviated via the introduction of elevated concentrations (10%) of CO_2 , which reduced the practicality aspect. Alternatively, the use of MICP enabled large crack repair without the need for any additional external CO_2 in this study, extending the range of applications in practice. As the healing efficiency of the bacteria-urea solution was much higher than those of air and water conditions, the healing duration could be shortened to less than 10 cycles to obtain a similar efficiency corresponding to complete healing.

6.3.1.2 Quantity and distribution of healing phases

As an important indicator of the extent of healing, it is necessary to assess the quantity and distribution of the precipitates in the whole specimen (Wang, Dewanckele et al. 2014). Accordingly, $\mu\text{-CT}$ was used on selected samples (i.e. those subjected to B-1U/A condition) to provide visualizations and quantification information on the internal structure of the matrix by generating three-dimensional (3D) images via the combination of a series of cross-

sectional (2D) images (Cnudde and Jacobs 2004, Wang, Dewanckele et al. 2014).

The analysis initiated by generating several cross-sectional 2D images (Fig. 6.18) that were used to create the 3D images of samples subjected to B-1U/A condition, as shown in Fig. 6.19. Every raw image presented a 2D array of contiguous squares consisting of 256 possible levels (i.e. 0-255 pixels) of gray intensity. The variations in the gray levels referred to different materials and were allocated as: (i) 0-30: Cracks and pores, (ii) 31-100: Healing products and (iii) 101-255: Cement matrix. The 3D view of the sample presented in Fig. 6.19 revealed that autogenous healing not only occurred on the top surface of the crack, but also throughout the crack depth, which was confirmed by the resonance frequency measurements reported in the subsequent section. The amount of precipitates (i.e. healing products) on the top surface was higher in comparison to the middle and bottom layers. This data was used to establish a relationship between the amount of precipitates as a function of crack depth, as shown in Fig. 6.20. As expected, the volume of healing products reduced as the crack depth increased, during which the precipitate content at the top surface was recorded to be ~78% higher than the amount at the bottom of the crack. These findings revealed that the top surface of the cracks were sealed quickly via the formation of precipitates such as hydrates and carbonates, whereas the healing process within the interior sections took longer as the crack depth increased.

Fig. 6.18 2D horizontal slices taken from the vertical direction of RMC-based blends subjected to B-1U/A condition, showing the (a) top, (b) middle and (c) bottom sections of the sample

Fig. 6.19 3D view of the spatial distribution around the crack of RMC-based blends subjected to B-1U/A condition

Fig. 6.20 Relationship between the precipitation content and crack depth in RMC-based blends subjected to B-1U/A condition

6.3.1.3 Resonance frequency (RF)

Serving as a non-destructive method, RF ratios (i.e. normalized with respect to the original/unloaded samples), shown in Fig. 6.21, were used to evaluate the healing recovery rate of RMC-based samples under different conditions. The initial RF ratios of the loaded samples (i.e. at cycle 0) were only ~70% of those of the original samples due to the formation of a number of cracks, which greatly reduced the stiffness of the samples. Even after 10 cycles, the RF recovery was very limited in samples subjected to A/A condition due to the lack of a continuous supply of water and sufficient CO₂ needed for hydration and carbonation processes. Offering a slightly improved scenario, samples subjected to W/A condition indicated a steady RF recovery when

compared to the original samples. This recovery was associated with the reduction in the crack widths during the curing process. However, the presence of several unhealed large cracks (Fig. 6.16(b) and 6.17(b)) even after 10 cycles led to lower RF values than those of the original samples before loading, which was consistent with the findings reported in Section 6.3.1.1.

Fig. 6.21 Normalized RF ratios of samples subjected to various conditions for up to 10 cycles

Differing from A/A and W/A conditions, the use of bacteria in the healing of cracked RMC-based samples under B-1U/A and B-2U/A conditions enabled all samples to achieve nearly 100% RF ratio recovery even after 2 cycles of healing. The B-1U/A group indicated a sudden jump in its RF ratio from 70% to almost 110% in the 2nd healing cycle, after which it remained almost stable until the end of 10 cycles. Alternatively, the B-2U/A group revealed a more gradual increase in its RF ratio over time. A possible explanation to this

difference in RF recovery could be related to the larger content of precipitates that formed on the top layer of the cracks due to large quantity of urea incorporated in the B-2U/A group. This may have increased the time it took for the bacteria-urea solution to penetrate into the deeper regions of the cracks and provide healing, leading to a stable growth of the RF ratio over time. When the B-1U/A and B-2U/A conditions were compared at the end of 10 cycles, it could be seen that both revealed very similar RF ratios, which highlighted that increased concentrations of bacteria-urea solution did not play a major role in the efficiency of healing within RMC-based samples once a sufficient level was achieved.

6.3.1.4 Microstructure

After all the samples were subjected to healing under various conditions, the phases (i.e. healing products) that formed within the cracks of selected samples were evaluated via microstructural analysis and elementary mapping, as shown in Fig. 6.22 and 6.23, respectively. The red lines used in Fig. 6.22 indicate the location and boundaries of cracks within each sample. Those subjected to W/A condition (Fig. 6.22(a)) led to the partial formation of a small amount of the crystals in the cracks, a majority of which was identified as brucite resulting from the hydration of RMC. This brucite was accompanied with a very limited quantity of rosette-like crystals (Fig. 6.22(b)), hinting the scarce formation of hydromagnesite, which was reported to have a similar morphology in previous studies (Davies and Bubela 1973, Li, Ding et al. 2003). The formation of hydromagnesite could be due to the limited amount of CO₂ in air used in W/A condition, during which most of the phases that formed within the cracks were widely scattered hydrates instead of carbonates.

When the samples subjected to B-1U/A and B-2U/A conditions were investigated, the dense formation of crystals within the cracks were observed. The morphologies of these crystals resembled HMCs. Samples subjected to B-1U/A regime indicated the formation of rosette-like hydromagnesite (Fig. 6.22(c)), whereas those under B-2U/A regime led to the formation of needle-

like nesquehonite (Fig. 6.22(d)) (Davies and Bubela 1973). The elemental mapping of these samples demonstrated in Fig. 6.23 illustrated the presence of Mg, O and C; and the absence of Si (i.e. from FA used as a raw material in the initial mix design); confirming the formation of carbonate phases as the main healing products after 10 cycles of healing in the bacteria-urea solution. These results confirmed the findings presented in Sections 6.3.1.1-6.3.1.3, highlighting that the extent of healing and the associated formation of carbonate phases was much more extensive under bacteria-urea solution in comparison to other conditions. This improvement in the healing process achieved via the use of the bacteria-urea solution could be attributed to the larger volumetric expansion associated with the formation of HMCs in contrast with brucite or unreacted MgO (Shand 2006).

Fig. 6.22 Microstructural images of the healing products that formed in the cracks of RMC-based blends under (a) and (b) W/A, (c) B-1U/A and (d) B-2U/A conditions

Fig. 6.23 Distribution of the element C, O, Mg and Si (colored region and black region indicate the presence or absence of the element) within the healing products that formed in the cracks of RMC-based blends under (a) B-1U/A and (b) B-2U/A conditions through elemental mapping

6.3.2 Discussion

The use of MICP in PC-based mixes relies on the formation of precipitates in a calcium-rich environment, during which bacterial cell walls with negative charges attract the Ca^{2+} in the solution to react with the generated CO_3^{2-} . This reaction leads to the formation of CaCO_3 on the cell surface, which acts as nucleation sites for the further growth of healing products (Douglas and Beveridge 1998). A similar mechanism was observed in RMC-based mixes prepared in this study, in which the bacteria penetrated into the cracks and attracted Mg^{2+} leaching from the bulk paste. This was followed by the reaction of Mg^{2+} ions with CO_3^{2-} in the presence of water to form a series of HMCs, which acted as nucleation sites for further growth, as shown earlier in Equations 2.20 and 2.21. Similar reactions were proposed in PC-based systems (Van Tittelboom, De Belie et al. 2010).

Investigation of the precipitation process via μ -CT and SEM-EDX analyses revealed the formation of HMCs first at the internal surface of the crack, followed by the subsequent filling of the crack when subjected to the bacteria solution. Generally, nucleation can be divided into “homogenous nucleation” and “heterogeneous nucleation”. Compared with heterogeneous nucleation, homogenous nucleation is always more difficult to take place due to the free energy barrier (Anisimov 2003). Under supersaturation conditions, homogenous nucleation mainly involves the formation of new phases via the fluctuations within the old phase (Oxtoby 1992); whereas heterogeneous nucleation takes place only at certain preferential locations via the seeding of the nuclei of new phases into the original/existing phases (Anisimov 2003). In this study, the solid phases (e.g. MgO or brucite) at the internal surfaces of the cracks of RMC-based samples acted as preferential locations due to the smaller amount of free energy required, thereby leading to the heterogeneous nucleation of the healing products and accelerating the kinetics of healing. When the ion concentrations in the cracks reached the saturation point, the initial deposition of HMCs started at the internal surface of the cracks. These

initial formations acted as nucleation sites for the subsequent formation of HMCs until final crack closure. The details of this procedure are provided in Fig. 6.24, where an illustration of the formation of healing products within the cracks of RMC-based blends under bacteria-urea solution is demonstrated.

Fig. 6.24 Illustration of the formation of healing products within the cracks of RMC-based blends subjected to bacteria-urea solution

Crack openings subjected to various self-healing regimes are usually studied via optical microscopy, which is a convenient method that provides visual information on the change of crack widths. However, the information obtained via these visual methods is mainly focused on the top surface of the cracks instead of the internal structure within the crack. This issue can be resolved via the use of additional techniques such as μ -CT and EDX, which enable the identification and quantification of the healing products in the deeper regions. Further information on the chemical compositions of the healing products and

the distribution of precipitates as a function of crack depth can facilitate an improved understanding of the healing mechanism throughout the sample cross-section. In this study, the findings emerging from these analyses have demonstrated that the extent of healing depends on the crack depth, even in situations where the samples are fully submerged into a solution as a part of the healing process. The heterogeneous self-healing observed in cracks is possibly related to the rapid formation of HMCs on the top surface. Due to the high activity of bacteria used in this study, the precipitates, once formed, rapidly sealed the top layer of the crack, slowing down the access of the bacteria-urea solution to the deeper regions. This sealed region created a barrier, which made it more difficult for the bacteria-urea solution to traverse through and reach the deeper regions of the crack, therefore reducing the amount of precipitates and increasing the time it takes for the complete healing of cracks at higher depths.

The main carbonate phase observed in the B-1U/A group was identified as hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$), whereas nesquehonite ($\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2(\text{H}_2\text{O})$) was dominant as the main healing product in the B-2U/A group. This variation on the type of HMCs in each group could be attributed to the pH values (Fig. 6.25), which varied in line with the different concentrations of urea present in the solution. Accordingly, it is known that pH values greatly influence the precipitation of HMCs (Zhang, Zheng et al. 2006, Ferrini, De Vito et al. 2009). In a low pH environment, bicarbonate ion (HCO_3^-) is more common than CO_3^{2-} and pH value significantly restricts the nucleation rate of Mg^{2+} and CO_3^{2-} as many CO_3^{2-} ions exist in the form of HCO_3^- (Zhang, Zheng et al. 2006). Previous studies (Hales, Frost et al. 2008) have reported that HCO_3^- and OH^- bands could be observed when nesquehonite ($\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2(\text{H}_2\text{O})$) was analyzed via Raman spectroscopy. Within the samples prepared in this study, those in the B-2U/A group led to lower pH than others due to the higher content of urea and bacteria activity. In this environment, the rapid consumption of a large amount of urea by bacteria led to the release of a higher amount of CO_2 within a short

time, which resulted in lower pH values and abundant presence of HCO_3^- within the cracks of B-2U/A samples, favoring the formation of nesquehonite (Equations 6.1 and 6.2). On the other hand, when the pH of the solution increased due to the lower content of urea involved in bacterial consumption, HCO_3^- ions were converted into CO_3^{2-} ions, which favored the formation of hydromagnesite (Equations 6.3 and 6.4).

Fig. 6.25 pH values of the powders extracted from the cracks of RMC-based blends (free of crystals formed within cracks) under different healing conditions

The transformation between hydromagnesite and nesquehonite has been investigated by a number of studies (Davies and Bubela 1973, Zhang, Zheng et al. 2006, Rheinheimer, Unluer et al. 2017), where it was reported that nesquehonite could convert into hydromagnesite at increased temperatures as a result of reduced water activity. However, the changes between nesquehonite and hydromagnesite with the variation of pH values have not been fully investigated. For a quick demonstration on the effect of pH, a commercial hydromagnesite powder was subjected to B-2U/A condition for the same duration (i.e. 10 cycles) as the RMC-based samples prepared earlier. After thoroughly washing with distilled water in an ultrasonic bath (i.e. to remove NH_4^+ ions) and vacuum drying, samples were analyzed under XRD. Fig. 6.26 shows the XRD patterns of the original hydromagnesite powder as well as the final powder after its curing under B-2U/A condition. The obtained patterns clearly indicated the presence of nesquehonite after the curing process, demonstrating that a portion of hydromagnesite was converted into nesquehonite during the B-2U/A regime. This transformation of hydromagnesite to nesquehonite could indicate that even if hydromagnesite precedes the formation of nesquehonite in RMC-based samples, it eventually converts into nesquehonite at lower pH values, which was the final phase observed in the cracks of samples under B-2U/A condition. Similar findings were also reported in (Zhang, Zheng et al. 2006), where it was shown that when the pH decreased under constant temperature, the major type of HMCs precipitated in solution changed from hydromagnesite to nesquehonite. A summary of the formation and transformation of different phases under the two different bacteria solutions used in this study is provided in Fig. 6.27.

Fig. 6.26 Major peaks of commercial hydromagnesite before and after its curing under B-2U/A condition (H = Hydromagnesite, N = Nesquehonite) via XRD patterns

Fig. 6.27 Illustration of the formation of different healing products within the cracks of RMC-based blends under different conditions

6.3.3 Conclusion

1. Compared with conventional MICP, the Mg-based MICP approach adopted in this study did not involve the use of additional Mg^{2+} as an ingredient, therefore increasing the cost-effectiveness and ease of practical application.

2. When compared to air and water-based curing, the use of bacteria-based curing led to a higher extent of autogenous healing by healing even the larger cracks after a few cycles. The major healing products within the cracks of samples subjected to bacteria-urea solution were identified as two commonly observed HMCs, nesquehonite and hydromagnesite. The formation and stability of these phases depended on the pH within the cracks. Accordingly, nesquehonite was observed in lower pH environments linked with high bacteria-urea concentration, whereas hydromagnesite was the main phase when the pH increased under lower bacteria-urea concentration. These healing products sealed the top layer of the cracks rapidly, which led to the partial isolation of the deeper crack regions from the bacteria-urea solution, increasing the time it took for complete healing and reducing the amount of precipitates at greater crack depths.

3. Regardless of this process, the use of bacteria-based curing generally led to the complete healing of even large cracks. The implementation of MICP on a large scale can provide an effective approach with respect to crack repair, enabling improved durability and performance in RMC-based blends.

Chapter 7 LIFE CYCLE ASSESSMENT OF THE PRODUCTION AND USE OF RMC AS A BINDER IN CONCRETE MIXES

This chapter focused on the investigation of the environmental impacts of RMC production. The obtained results were compared with the production and use of PC using a LCA approach. This part of the study assessed the environmental impacts of RMC production and compared the obtained results in terms of the different impact categories and key parameters with those used in the production of PC. The details of the methodology used (i.e. goal, functional unit, scope, inventory and impact assessment) for the LCA of RMC and PC production and use were provided in the following Sections 7.1-7.4.

7.1 Life cycle assessment

The LCA methodology utilized in this study was based on the International Organization for Standards (ISO) 14040 (ISO14040 2006) as used by several previous studies (Chen, Habert et al. 2010, Valderrama, Granados et al. 2012, Li, Zhang et al. 2015). The LCA software SimaPro 7.0 was used to evaluate the environmental impacts of inventory elements and present a comparison of PC and RMC production routes through the 4 main stages below:

- 1) Selection of scope and system boundaries for assessment
- 2) Choice of products and process inventory (i.e. inputs and outputs)
- 3) Evaluation of environmental impact data compiled in the inventory
- 4) Interpretation of results and recommendations for improvement

7.2 Goal, functional unit and scope

The goal of this study was to assess the environmental impacts of RMC production and compare the outcomes with traditional PC production. The LCA of the main processes was investigated from a 'cradle-to-gate' perspective consisting of relevant environmental procedures ranging from the

acquisition of raw materials to the packaging of the final product (ISO14040 2006). The major materials and process flow diagrams showing the energy and heat consumption of PC and RMC production processes are shown in Fig. 7.1, respectively. As can be seen in Fig. 7.1, RMC production involves the use of a single ingredient (magnesite), presenting a simpler approach to raw material acquisition when compared to PC production, which involves the acquisition and use of several raw materials.

(a)

(b)

Fig. 7.1 Material flow diagram for the production of 1 tonne of (a) PC and (b) RMC (Huntzinger and Eatmon 2009, Li, Zhang et al. 2015)

Regarding the cement production, the functional unit of assessment used in this study was 1 tonne of cement (PC or RMC). The end products used for comparison purposes in the model were traditional PC (produced in the USA and Europe) and reactive MgO cement (RMC) (produced in China). The inventories for PC production vary among different countries and regions, which can affect the comparison between PC and RMC production. The main differences between the two PC sources are the quantity of raw materials and the type and quantity of energy profile used during the production process. These variations, which are influenced by the availability of different technologies and policies in different countries, result in different emissions data. The scope of the comparative LCA showing the system boundaries comprising the most significant procedures involved in the production of each material is indicated in Fig. 7.2. This process can be generally divided into three main stages for both types of cement as: (i) Raw materials quarrying; (ii) clinker production at the plant (including the mixing and calcination of all raw materials) and (iii) grinding and crushing of clinker. Compared with RMC, an extra step involving the addition of gypsum to control the setting of PC is included in the third stage.

Fig. 7.2 Scope of comparative LCA showing the production processes of (a) PC and (b) RMC (Huntzinger and Eatmon 2009, BREF 2010)

7.3 Life-cycle inventory

As there are no inventories for magnesite mining in the existing database in SimaPro 7, the input and emissions data for the production of 1 tonne of reactive MgO cement (RMC) presented in Table 7.1 was derived from the supporting information provided in (Li, Zhang et al. 2015). Inventory data for the procurement of raw materials (e.g. quarrying of limestone), together with energy (electricity and heat) consumption of different procedures, was acquired from the SimaPro database. The details of raw materials, energy consumption and emissions for the production of 1 tonne of traditional PC (USA and Europe) are outlined in Table 7.2. The CO₂ emissions associated with PC and RMC production are reported as 0.78-0.83 t/t and 1.1 t/t, respectively.

Table 7.1 Inventory for the production of 1 tonne of RMC (China)

Input/emissions	Amount (Li, Zhang et al. 2015)
Raw materials	
Magnesite (ton)	2.17
Water (ton)	0.01
Energy	
Coal (ton)	0.27
Electricity (kWh)	8.67
Diesel (ton)	0.54
Emissions	
CO ₂ (kg)	1096.54
SO ₂ (kg)	4.21
CO (kg)	0.02
NO _x (kg)	0.01
Water vapour (m ³)	0.01
Magnesite dust (kg)	0.99

Table 7.2 Inventory for the production of 1 tonne of PC

Input/emissions	Amount for PC (USA) (Marceau, Nisbet et al. 2006, Huntzinger and Eatmon 2009, Boesch and Hellweg 2010)	Amount for PC (Europe) (Spielmann, Bauer et al. , ATILH 2003, Josa, Aguado et al. 2004, Kellenberger, Althaus et al. 2007, Boesch and Hellweg 2010)
Raw materials		
Limestone (ton)	1.27	1.32
Clay (ton)	0.10	0.32
Sand (ton)	0.04	0.07
Iron ore (ton)	0.03	0.01
Gypsum (ton)	0.05	0.05
Water (ton)	0.01	0.53
Energy		
Coal (ton)	0.12	5.53E-9
Fuel oil (ton)	7.47E-4	1.53E-9
Natural gas (m ³)	3.75	-
Gasoline (litres)	0.11	-
Electricity (kWh)	150.00	71.92
Petroleum coke (ton)	0.01	0.10
Diesel (ton)	-	9.00E-7
Emissions		
CO ₂ (kg)	781.30	832.61
SO ₂ (kg)	1.33	0.63
CO (kg)	0.82	1.96
NO _x (kg)	2.57	1.79
Cement kiln dust (kg)	46.57	0.87
Particulate matter (kg)	1.13	0.03

7.4 Impact assessment in LCA

In this LCA study, Eco-indicator 99 was used as it enabled the selection of various indicators to quantify the environmental burdens of cement production across a wide range of categories. Problem-oriented (mid-points) and damage-oriented (end-points) were included in this method to incorporate major environmental impacts such as climate change and assess the damage of these environmental burdens on human health, eco-system quality and resources. The mid-points provided a well-defined and comprehensive profile of the ecological impact of RMC and PC production, whereas the end-points presented a clear analysis of the impacts of these processes on human health, eco-system quality and resources (Ortiz, Castells et al. 2009).

Damage oriented impacts considered in this LCA study were carcinogens, respiratory organics and inorganics, climate change, radiation, ozone layer, eco-toxicity, acidification/eutrophication, land use, minerals and fossil fuels. Mid- and end-point approaches were adopted to evaluate damage on human health, eco-system and resources (Eco-indicator 99, hierarchy version). In addition to damage assessment, normalization, the details of which are given in the Appendix, was incorporated in the analysis to reveal the exact influence of each of the impact categories on the whole environmental issue considered (Goedkoop, Schryver et al. 2010). A mixing triangle was used to address the weighting problems for the two products/processes, in which the indifference lines were computed by determining the points where they transverse the boundaries of the triangle (i.e. intersection points) (Hofstetter, Braunschweig et al. 1999). The details of the calculation of values for the mixing triangle are provided in the Appendix.

To enable this and explore the global warming potential of RMC and PC production, the effect of each binder on climate change was also investigated by IPCC 2007 within a timeframe of 100 years. The results obtained at the end of this analysis aim to improve the decisions of policy makers within the construction industry on a local and global level.

Any inaccuracies in the data within the inventories used in this analysis due to the differences in parameters such as maintenance and policy have the potential to greatly affect the outcome. Besides, inventories such as fuel and energy vary among regions and factories. Therefore, a sensitivity analysis is necessary to evaluate the accuracy of the assumptions and estimate the influence of the parameters used on LCA results (ISO 1997). This can be facilitated by scenario modelling (Huijbregts, Norris et al. 1999). The LCA for the production of RMC was performed by using a dataset from a Chinese RMC manufacturing plant (Li, Zhang et al. 2015). Any variations of the parameters within this dataset can result in different outcomes. Sensitivity

analysis involving the energy, raw materials and emissions associated with RMC production was investigated through scenario modelling to improve the LCA results against variations within these parameters.

Coal is the main fuel used in the production of RMC in China, whereas plants in Europe generally use natural gas, petroleum coke and fuel oil (BREF 2010). A change in the fuel type will also change the final LCA results. The sole use of coal in the large volume production of RMC in China may not reflect the environmental impact of RMC production on a global scale as other types of fuel can also be used in plants located in other countries. To obtain a full understanding of the implications of RMC production, two scenarios (Scenarios 1 and 2) in which other fuel types (i.e. coal gas and gasoline) replaced coal at a 30% substitution rate based on the total energy released by these fuels (ENS) were created. The inventories for coal gas and gasoline used in China were derived from the China Life Cycle Database (CLCD). This analysis revealed the sensitivity of final results to energy type. Variations in the amount of energy, emissions and raw materials used amongst different regions and plants due to the differences in local policies and technologies were also taken into account with the introduction of three additional scenarios (Scenarios 3-5). In these, the total amounts of energy, emissions and raw materials were systematically increased by 10% to analyze their effects on the production of RMC. Therefore, in addition to the base scenario in which coal is the only fuel used for the production of RMC, 5 separate scenarios were employed as below:

- 1) Scenario 1: 30% coal was replaced by gasoline (30% gasoline + 70% coal)
- 2) Scenario 2: 30% coal was replaced by coal gas (30% coal gas + 70% coal)
- 3) Scenario 3: Total amount of raw materials was increased by 10%
- 4) Scenario 4: Total amount of energy was increased by 10%
- 5) Scenario 5: Total amount of emissions was increased by 10%

7.5 Results and discussion

7.5.1 Environmental impacts of RMC and PC production

The damage assessment of individual environmental impacts of PC and RMC production is shown in Fig. 7.3. When compared to PC production, RMC production generates a larger proportion of carcinogens, which is mainly attributed to the high coal usage by MgO plants. RMC production presents an advantage in terms of radiation, ozone layer, eco-toxicity, acidification/eutrophication, minerals, and fossil fuels when compared to PC production, whereas its impact in climate change is higher. This is because climate change is associated with the total amount of CO₂ emitted during the production process. The decomposition of magnesite releases a higher amount of CO₂ than that of limestone used in PC production (~1.1 vs. 0.78-0.83 t/t), leading to a higher climate change score for RMC in spite of the lower production temperatures.

Fig. 7.3 Comparative impact category of cement production with respect to the greatest score among scenarios

Although PC-based mixes can also carbonate, unlike RMC-based mixes, this carbonation process can result in the loss of strength and is therefore not preferable (Liska and Al-Tabbaa 2009). This is because during carbonation, C-S-H is decalcified by the lowering of its Ca/Si ratio and the conversion into a highly porous and hydrous form of silica (Taylor 1997). Studies have shown that carbonation of C-S-H starts as soon as the majority of the available $\text{Ca}(\text{OH})_2$ has carbonated (Peter, Muntean et al. 2008). Therefore, carbonation of PC is not considered here as it results in a decline in the strength of PC formulations, which rely on the hydration process for strength gain.

Table 7.3 Environmental indicators of RMC and PC production

Impact category	Unit	RMC (China)	PC (USA)	PC (Europe)
Carcinogens	DALY ^a	2.30E-05	9.47E-06	1.24E-05
Resp. organics	DALY ^a	8.35E-08	1.93E-07	3.15E-07
Resp. inorganics	DALY ^a	5.00E-04	5.40E-04	3.30E-04
Climate change	DALY ^a	2.80E-04	2.00E-04	2.10E-04
Radiation	DALY ^a	3.29E-08	9.36E-07	5.76E-07
Ozone layer	DALY ^a	1.15E-09	2.98E-08	6.43E-08
Ecotoxicity	PAF*m ² *yr ^b	6.24	14.37	17.36
Acidification/ Eutrophication	PDF*m ² *yr ^b	7.29	20.21	14.14
Land use	PDF*m ² *yr ^b	8.37	5.15	4.98
Minerals	MJ surplus ^c	0.80	3.09	1.53
Fossil fuels	MJ surplus ^c	95.34	283.01	857.23

a: Damage to human health is associated with the loss of life years and the disability of quantity of years lived, expressed in terms of DALY (Disability Adjusted Life Years);

b: Damage to ecosystem quality is related with the extinction of species in a specific region for a specific period of time, expressed as PAF*m²*yr (Potentially Affected Fraction * m² * year) and PDF*m²*yr (Potentially Disappeared Fraction * m² * year)

c: Damage to resources is associated with the surplus energy required for the quarrying of minerals and fossil fuels in the future.

Another important impact category in cement production, acidification can cause serious damage to ecosystems, water supplies, soil and infrastructure (Valderrama, Granados et al. 2012). The alleviation of acidification in RMC production when compared to PC production is due to the lower calcination temperatures utilized in the former (~800°C vs. 1450°C). This results in a reduction in the amount of NO_x and SO₂ emissions, which account for 99% of the overall acidification issue (Josa, Aguado et al. 2007). This also explains the benefits of RMC over PC production in other environmental indicators (e.g. radiation, ozone layer and eco-toxicity etc.), the details of which are listed in Table 7.3.

Fig. 7.4 Normalized impact categories with respect to climate change set at 100%

Fig. 7.4 displays the results of all normalized environmental impact categories with respect to climate change set at 100%. This representation clearly identifies respiratory inorganics, fossil fuels and climate change as the three main impact categories in the production of both cement types. The end-point environmental impacts of RMC and PC production are shown in Fig. 7.5. RMC production presents a 6.4-31.2% higher damage to human health than

PC production. This is mainly due to the larger emissions of carcinogens associated with RMC production, which adversely affect human health. On the other hand, RMC production has a lower impact on the overall ecosystem quality and resources when compared to PC. This is attributed to the fact that RMC perform better in minimizing environmental factors such as acidification, land use and eco-toxicity, which contribute to the overall damage to ecosystems and resources.

Fig. 7.5 Comparative damage categories with respect to the greatest score among scenarios

A weighting process is essential for the determination of the preferred cement type according to the overall environmental burdens of each binder. Single score, which reflects the sum of scores obtained under each impact category, is one of the methods used to evaluate the environmental burden of different products. It is calculated by adding up the scores obtained by each binder under all impact categories (e.g. climate change, fossil fuels, carcinogens etc.) used in their environmental assessment. Although there are some

disagreements with the use of single score due to the subjectivity of the selection of the respective weighting factors with varying impacts (Finnveden, Hauschild et al. 2009), it can present a clear profile of the LCA results to decision makers if its limitations are recognized and acknowledged. Within this system, a lower single score refers to a lower environmental burden during cement production and vice versa. Accordingly, the single score of RMC is calculated as 24.38 points, which is lower than the scores of PC USA and Europe recorded as 28.39 and 36.39 points, respectively. This reveals an up to 33% lower score for RMC, highlighting the lower environmental impacts of RMC production when compared to PC production.

The impacts of each type of cement on human health, ecosystem quality and resources as a whole were also evaluated on a mixing triangle. This method improves the clarity of the weighting procedures by resolving the weighting problems more effectively than the single score approach, thereby facilitating better decision making. Fig. 7.6(a) and (b) present the mixing triangle results for RMC and PC production, demonstrating the indifference line and the corresponding subareas with their specific grading orders. The right side of the indifference line corresponds to the weighting sets where RMC has a lower environmental impact than PC from both sources (USA and Europe). Nearly 90% of all the possible weighting sets indicate RMC production as the environmentally superior and preferable option when compared to PC production.

(b)

Fig. 7.6 Mixing triangle showing a comparison between RMC (China) and (a) PC (USA), and (b) PC (Europe)

7.5.2 Sensitivity analysis of RMC production

Table 7.4 shows the variations in the environmental impacts within the five scenarios analyzed under the sensitivity analysis. The first two scenarios include the use of different fuel combinations in the production of RMC. The partial replacement of coal by gasoline and coal gas led to substantial reductions of up to ~27% in the amount of carcinogens. An increase in the amount of respiratory organics was observed when coal was replaced by gasoline. This was associated with the large emission of particulate matters during the refinery of crude oil. Changing the fuel type had a negligible effect on the amount of respiratory inorganics, acidification/eutrophication and climate change. The reason climate change was not as sensitive to the fuel type is because the CO₂ emitted during the calcination of magnesite is the major contributor to climate change, which is independent of the fuel type used. The use of alternative fuels to partially replace coal reduced the damage to ozone layer, ecotoxicity, land use and minerals by 20-93%. The partial replacement of coal with gasoline resulted in an increase in the fossil fuels, whereas a small variation was observed when coal was replaced by coal gas. This is expected as coal gas is produced from coal and steam water, resulting in a similar fossil fuel consumption as coal. The use of gasoline induced an increase in the amount of radiation, which may be due to the emission of radioactive elements (e.g. radon) during the refinery of crude oil used for the production of gasoline.

Table 7.4 Sensitivity analysis of the environmental impacts of RMC production under scenarios 1-5 relative to the base scenario

Impact category	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
Carcinogens	DALY ^a	-27.34%	-21.70%	0.06%	9.94%	0.00%
Resp. organics	DALY ^a	381.96%	-19.20%	0.13%	9.87%	0.00%
Resp. inorganics	DALY ^a	-12.93%	7.70%	0.04%	5.32%	4.64%
Climate change	DALY ^a	-3.42%	6.24%	0.01%	1.81%	8.18%
Radiation	DALY ^a	65.17%	-25.28%	0.34%	9.66%	0.00%
Ozone layer	DALY ^a	-21.61%	-21.61%	2.31%	7.69%	0.00%
Ecotoxicity	PAF*m ² *yr ^b	-92.58%	-25.84%	0.19%	9.81%	0.00%
Acidification/ Eutrophication	PDF*m ² *yr ^b	-6.83%	0.06%	0.13%	3.87%	6.01%
Land use	PDF*m ² *yr ^b	-40.51%	-29.16%	0.03%	9.97%	0.00%
Minerals	MJ surplus ^c	-27.55%	-28.46%	0.06%	9.94%	0.00%
Fossil fuels	MJ surplus ^c	337.89%	1.55%	0.42%	9.58%	0.00%

a: Damage to human health is associated with the loss of life years and the disability of quantity of years lived, expressed in terms of DALY (Disability Adjusted Life Years);

b: Damage to ecosystem quality is related with the extinction of species in a specific region for a specific period of time, expressed as PAF*m²*yr (Potentially Affected Fraction * m² * year) and PDF*m²*yr (Potentially Disappeared Fraction * m² * year)

c: Damage to resources is associated with the surplus energy required for the quarrying of minerals and fossil fuels in the future.

Scenarios 3-5 show the influence of increasing the raw materials, energy and emissions by 10%, respectively. Increasing the quantity of raw materials had a negligible effect on the overall environmental impact of RMC production. Energy was identified as the key parameter among the parameters investigated as it had the highest influence on the environmental burdens of RMC production. An average increase of ~10% was observed in most impact

categories with an increase in the amount of energy, showing that a majority of the environmental impacts is mostly dependent on the amount of energy utilized during the production process. Climate change remained relatively unaffected as the calcination process is the main contributor to emissions. Increasing emissions by 10% had a direct effect on climate change as expected and led to an ~8% increase, whereas most of the other impact categories remained relatively unaffected.

The variations in damage impacts within scenarios 1-5 with respect to the base scenario used in the production of RMC are shown in Table 7.5. Partial replacement of coal with gasoline significantly increased the damage to resources as the refinery of crude oil requires the consumption of a large quantity of minerals and fossil fuels. However, the use of gasoline alleviated the damage to human health as it decreased the amount of carcinogens and respiratory inorganics when compared to coal usage. An increase in the damage to human health and a decrease in the damage to ecosystem quality were observed when coal was replaced with coal gas. This replacement did not have a considerable effect on resources as both fuel types are obtained from the same material group. Scenarios 3-5 involving a 10% increase in raw materials, energy and emissions indicated variable effects on each damage category. While changing the amount of raw materials did not influence the damage impacts on any of the categories investigated, increasing the energy amount increased the damage to ecosystem quality and resources by 7% and ~9%, respectively. Emissions had a direct influence on human health, causing a ~6% increase, which was related to the increase in the amount of respiratory inorganics.

Table 7.5 Sensitivity analysis of the damage impacts of RMC production under scenarios 1-5 relative to the base scenario

Damage category	Unit	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
Human Health	DALY	-9.95%	6.34%	0.03%	4.04%	5.75%
Ecosystem Quality	PDF*m ² *yr	-24.87%	-15.95%	0.08%	6.98%	2.69%
Resources	MJ surplus	334.84%	1.30%	0.42%	9.41%	0.00%

Scenario modelling was also applied for the calculation of single scores shown in Fig. 7.7. When compared to the base scenario in which all the energy needed for the production of RMC was supplied by coal sources, the replacement of 30% of coal with gasoline and coal gas led to ~22% and ~5% increases in the overall environmental impact of RMC production, respectively. The higher sensitivity of the results to the replacement of coal by gasoline as opposed to coal gas was due to the different raw materials used in the production of these two energy sources. Increasing the amount of raw materials by 10% did not change the score at all, whereas increases in the energy and emissions led to a 4-5% increase in the overall environmental score. Except for scenario 1 in which coal was partially replaced by gasoline, the scores of all the scenarios presented in this study (24.38-25.61) were lower than that of PC (28.39 and 36.39). This indicates the lower impact of RMC production on the environment under different scenarios when compared to PC production.

Fig. 7.7 Environmental impacts of base scenario and scenarios 1-5 used for the production of RMC presented in terms of a single score

7.6 Conclusion

1. Production of RMC from the calcination of magnesite outperformed PC production in mitigating the majority of environment impacts imposed on the ecosystem and resources. The main disadvantage of RMC production when compared to that of PC was its effect on human health, which was attributed to the large quantity of coal used in the production of RMC.

2. The decomposition of magnesite released a higher amount of CO₂ than that of limestone used in PC production (~1.1 vs. 0.78-0.83 t/t), leading to a higher climate change score for RMC in spite of the lower production temperatures.

3. Scenario modelling indicated that the overall environmental impact of RMC production was significantly affected by the type and amount of energy utilized during this process. Partial replacement of coal by gasoline led to an increase in the overall environmental burdens. Although the Chinese production and manufacturing industries mainly utilize coal as their primary energy supply, other energy types such as gasoline and natural gas were also used at smaller percentages.

Chapter 8 CONCLUSIONS AND FUTURE PLANS

8.1 Conclusions

The use of air-entrained agent, mix design optimization, industry waste and calcined dolomite all succeeded in improving the mechanical properties, carbon sequestration and sustainability of RMC formulations. Meanwhile, strain-hardening and self-healing behaviors were also observed when PVA fibers were introduced into RMC formulations. The conclusions indicate that the project objectives have been sufficiently achieved. Below is a summary of the main conclusions generated from each study performed under this research.

8.1.1 Influence of mix design and use of additives on the mechanical performance and carbon sequestration of RMC formulations

8.1.1.1 Influence of mix design (i.e. water, cement and aggregate contents)

The initial water content was determined as the main parameter controlling the final properties of RMC samples. The compressive strength of RMC samples increased with a reduction in the w/c ratio. This was associated with lower porosities of the drier samples, along with the faster diffusion of CO₂ within dry mediums. Another factor that contributed to the mechanical performance of RMC samples was the morphology of the formed carbonates, rather than their quantity. The densification of the sample microstructures, enabled via the formation of hydrate and carbonate phases that filled in the initially available pore space, was an indication of the extent of the carbonation reaction.

8.1.1.2 Influence of use of AEA

The inclusion of AEA increased the workability, long-term compressive strength and thermal conductivity of RMC samples as it facilitated CO₂ diffusion, while inhibiting water penetration and heat transfer. The key factors that controlled the overall strength development of RMC samples were determined as the initial sample porosity, controlled by the AEA and water contents, and curing conditions (i.e. availability of CO₂).

8.1.1.3 Influence of different contents of industrial by-products (i.e. PFA and GGBS)

While the use of both PFA and GGBS in RMC samples led to smaller initial porosity and water sorptivity values due to their finer natures, RMC-PFA samples achieved the lowest porosity values amongst all samples at the end of 28 days. This reduction in the porosity of RMC samples was in agreement with their steady strength development that led to 28-day strength values of 45 MPa, which were lower than those obtained by PC samples via hydration (55 MPa). However, the introduction of PFA in RMC formulations revealed higher strengths (60 MPa) than both the RMC and PC samples. These improvements were associated with the densification of samples containing PFA or GGBS because of the filler effect as well as the pozzolanic reactions that led to the formation of hydrate phases, thereby reducing the initial porosity.

8.1.2 Use of calcined dolomite as a new RMC source

8.1.2.1 Influence of various contents of calcined dolomite replacements on the mechanical performance and carbon sequestration of RMC formulations

The main factors that determined the performance of RMC formulations were the MgO, dolomite and water contents within the initial mix design. These factors influenced the initial porosity as well as the degree of carbonation and the morphology of the final carbonate phases. Samples involving the

simultaneous use of RMC and dolomite led to improved performance when compared to others, revealing 28-day strengths as high as 57 MPa, which were up to 60% higher than the control samples containing only MgO or dolomite. Dolomite can be used as a new type of raw material for RMC source without sacrificing the mechanical performance, and the cost of RMC was greatly reduced.

8.1.2.2 Mechanical performance and carbon sequestration of RMC and calcined dolomite formulations under different curing conditions

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.

8.1.3 Development of RMC-based strain-hardening composites with the ability to undergo self-healing

8.1.3.1 Strain-hardening behavior of RMC formulations

Adequate binder content and w/b ratio was necessary for desirable fiber dispersion. Lower water contents and longer curing ages contributed to the strength development of RMC-SHC by improving the fiber-matrix interface bond and enhancing the formation of a dense carbonate network.

8.1.3.2 Self-healing behavior of RMC formulations

(i) Water and CO₂-based self-healing behavior

Crack sealing and a significant mechanical recovery can be realized through

proper environmental conditioning. The presence of water was necessary to enable autogenous healing. Elevated CO₂ concentrations led to the formation of HMCs that were useful in sealing larger cracks. However, ample supply of CO₂ resulted in a fast sealing of the cracks on the near surface regions, creating barriers for further carbonation and healing of the inner sections of the cracks.

(ii) Bacteria-based self-healing behavior

This study investigated the feasibility of crack healing by means of microbial induced carbonate precipitation (MICP) in RMC-based blends. Pre-cracked samples were subjected to four different healing conditions involving air, water and two different bacteria-urea concentrations. Different types of HMCs formed under each bacteria-urea solution due to differences in pH associated with bacteria-urea concentrations. While these phases first formed on top of the cracks, investigation of the crack depth revealed the presence of precipitates at inner sections, albeit at lower contents. The adopted MICP approach leading to the production of HMCs was an effective method for healing cracks in RMC-based samples, resulting in a high extent of healing in a short time period.

8.1.4 Life cycle assessment of the production of RMC

Production of RMC from the calcination of magnesite outperforms PC production in mitigating the majority of environment impacts imposed on the ecosystem and resources and scenario modelling indicated that the overall environmental impact of RMC production is significantly affected by the type and amount of energy utilized during this process.

8.2 Future work

This study contributed to the literature via the information generated on the relationship between the fresh and hardened properties of RMC formulations. This involved the identification of the influence of phase formations on the

mechanical and microstructural development of RMC samples. This study is novel as it is the first in the literature to investigate the environmental impacts of the production and use of RMC as a binder in comparison with PC, introduce several additives (AEA, PFA and GGBS) and alternative sources for magnesium (calcined dolomite) into RMC mixes and develop RMC-based strain hardening composites with the ability to undergo self-healing. The reported findings have indicated the high potential of RMC-based formulations to be used in various building applications based on their ability to be produced from alternative sources and gain strength via the sequestration of CO₂. Further work to be performed in the following two areas can improve the use of RMC as a binder and enhance the overall mechanical performance and sustainability aspects of the developed formulations.

8.2.1 Analysis of the properties and application of RMC synthesized from reject brine

The amount of waste brine generated is increasing on a global level due to the rising demands of the growing world population on clean water supplies. The use of desalination plants to generate drinking water is becoming more common in contributing to the supply of clean drinking water around the world. The highly saline effluent from the desalination process not only has no economic value, but also has adverse effects on the marine ecosystem as it is currently discharged back into the sea at the end of the desalination process. This process disturbs the local water and sediment by introducing a multi-component waste and increases the temperature, meanwhile endangering the marine organisms due to the residual chemicals mixed into the brine from the pre-treatment process.

Production of RMC from reject brine provides a new purpose for this otherwise harmful waste material and proposes a sustainable alternative for the current production of RMC from magnesite. There are currently no studies on the performance of RMC derived from reject brine as a binder in concrete

formulations. The identifications of the properties of RMC via a detailed analysis can enable its recommendation in various building applications and increase the overall sustainability of the formulations it is incorporated in.

8.2.2 Investigation of the different uses of dolomite within concrete formulations

The use of dolomite in alkali-activated cement systems involving a mix of dolomite and bentonite subjected to calcination under high temperatures (e.g. 1100–1200°C) has been reported in recent studies (Peng, Wang et al. 2017)). Another study (Szybalski and Nocuń-Wczelik 2015) investigated the role of dolomite on the hydration of cement, in which dolomite was added as an active ingredient or as a cement replacement at low dosages. Half-burnt dolomite, composed of MgO and CaCO₃, has also been used as a supplementary cementitious material (SCM) to partially replace PC. Other than its use as an additive within the binder content, raw dolomite extracted as a natural resource can also be used as a coarse aggregate within concrete mixes (Prokopski and Halbiniak 2000), incorporating both RMC and/or PC as the main binder. Therefore, the feasibility of developing sustainable concrete formulations involving the use of natural dolomite within the aggregate profile can be investigated under various curing conditions to improve not only the mechanical performance (i.e. via the presence of MgO and CaO within dolomite available for reaction) but also the sustainability aspect of the final mixes.

8.2.3 Comparison between mechanical performance, carbon sequestration and environmental impacts of RMC and PC formulations containing high volume of SCMs

PC formulations containing high volume of SCMs has been investigated in a number of studies owing to their superior mechanical performance and durability (Li and Zhao 2003, Lammertijn and De Belie 2008), meanwhile, it was also indicated that with the use of industry waste as clinkers, the

environmental impacts of PC production will be greatly reduced (Huntzinger and Eatmon 2009). Therefore, in the future, a more comprehensive comparison between PC and RMC containing high volume of PFA or GGBS should be performed in terms of their mechanical performance, carbon sequestration and environmental impacts.

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