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UNIVERSITY**

SINGAPORE

**IMPROVING THE STRENGTH AND MICROSTRUCTURE OF
REACTIVE MAGNESIA BASED CONCRETE BLOCKS**

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**Interdisciplinary Graduate School
Energy Research Institute @ NTU**

2018

IMPROVING THE STRENGTH AND MICROSTRUCTURE OF REACTIVE MAGNESIA BASED CONCRETE BLOCKS

PU LIYUN

INTERDISCIPLINARY GRADUATE SCHOOL

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

2018

Statement of Originality

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

10 Aug 2018

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Date

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Pu Liyun

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.

10 Aug 2018

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This thesis contains material from (a) paper(s) published in a/the following peer-reviewed journal(s) where I was the first and/or corresponding author.

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The contributions of the co-authors are as follows:

- Dr. Cise Unluer provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr. Cise Unluer.
- I co-designed the study with Dr. Cise Unluer and performed all the laboratory work at the School of Civil and Environmental Engineering. I also analyzed the data.
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Abstract

The cement industry is a major source of CO₂ emissions as the production of Portland cement (PC) accounts for 5-7% of anthropogenic CO₂ emissions. Reactive magnesium oxide (MgO) cements with lower energy requirements and CO₂ emissions have been proposed as an alternative binder. They are produced at lower temperatures than PC (~750 vs. 1450 °C), offer improved durability (e.g. against acid and sulfate attacks) due to the low solubility of their hydration products and gain strength via carbonation when MgO is used as a binder. A very limited amount of work has been reported on the carbonation degree, performance and durability of MgO cement concrete under various conditions. In order to fill this gap, the main goal of this research is to (i) enhance the carbonation, mechanical performance and microstructural development of MgO cement concrete containing different additives, (ii) evaluate the stability of the formed phases under various conditions involving high temperatures and aggressive environments, and (iii) provide a comparison between commercial and lab scale blocks in terms of performance and microstructure.

In line with these goals, initial studies focused on evaluation of the influence of various concrete mix designs on the carbonation and mechanical performance of MgO cement concrete. A novel pre-conditioning technology was used to improve the strength development of MgO cement. Furthermore, the performance and stability of phases in MgO cement concrete subjected to high temperatures of up to 550 °C and various aggressive environments were investigated. Pulverized fly ash (PFA) and ground granulated blast-furnace slag (GGBS) were introduced as supplementary cementitious materials (SCMs) to investigate their influence on MgO cement concrete. Finally, the difference between MgO-based lab-scale and scaled-up concrete blocks were evaluated in terms of their mechanical performance and microstructural development. These results were compared with those of the concrete block trials conducted in a commercial lab. In all studies, the performance of the prepared blocks was evaluated in terms of density, porosity and compressive strength measurements. Hydration and carbonation of MgO was studied by isothermal calorimetry, pH measurements, phenolphthalein test, hydrochloric

acid test and microstructural analysis. The identification and quantification of relevant phases were performed by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX).

In the initial studies, the results indicated the progress of carbonation depended on the cement and water contents, in which MgO content of 10% and water to cement (w/c) ratio of 0.8 resulted in best mechanical performance. The main carbonation product, hydromagnesite, started forming on the outer depths of concrete and gradually proceeded towards the inner cores. The fibrous structure of hydromagnesite demonstrated interlocking properties, which are known to provide outstanding strength in MgO cement concrete when compared to PC. 10% CO₂ curing was proved to be an ideal condition for the strength gain of MgO cement. Pre-conditioning process under 60 °C and RH of 90% enhanced the carbonation process. Further studies investigated the performance of MgO cement under high temperatures (i.e. 40-550 °C) and four types of chemical attack (i.e. chloride penetration, sulfate attack, freeze-thaw cycling, and seawater exposure) for up to 6 months. Results showed that the hydration and carbonation products remained relatively stable until 350 °C, during which a minor strength reduction was observed. MgO cement concrete containing SCMs such as PFA and GGBS indicated better durability over PC concrete under chloride and sulfate attacks and freeze-thaw cycling. Finally, scaled-up MgO cement concrete blocks revealed a satisfactory mechanical performance in spite of their lower carbonation degrees when compared to lab-scale blocks.

The overall study clearly revealed the influence of key parameters such as concrete mix design and curing conditions on the performance and microstructural development of MgO-based concrete blocks, as well as the durability and the scaling up feasibility of the developed formulations. Comparison of MgO-based blocks with corresponding PC-based blocks were provided in terms of performance. These results were further supported with the quantitative analysis of the hydrate and carbonate phases present in each system. The presented findings did not only facilitate the understanding and controlling of the properties that affect the performance and microstructure of MgO cement-based mixes, but also demonstrated the potential of commercial MgO cement-based concrete.

Lay Summary

The extensive use of Portland cement (PC) contributes to global warming due to the high CO₂ emissions associated with its production. To overcome this issue, several sustainability initiatives have been introduced, focusing on the development of novel cements with lower energy requirements and CO₂ emissions. One example of such cements with a significant sustainability potential over traditional PC is reactive magnesia (MgO) cement. MgO cement can be produced at much lower temperatures than PC (700 vs. 1450 °C), sequester CO₂ and obtain outstanding mechanical performance throughout the carbonation process, and can be fully recycled at the end of use. The major goal of this research project is to enhance the performance and microstructure of MgO cement-based formulations.

Hydration, which involves the reaction of water with the cement component in concrete; and carbonation, which involves the reaction of CO₂ with the cement component and water in concrete are two important processes for the strength development of PC and MgO cement-based mixes, respectively. MgO cement is found to gain strength in elevated CO₂ concentrations. In the presence of sufficient water, brucite (i.e. the main hydration product of MgO cement) reacts with CO₂, leading to the formation of hydrated magnesium carbonates (HMCs). Carbonation is a critical process for MgO cement binders as they harden and gain strength via the formation of HMCs. The carbonation of MgO cement is controlled by many factors such as mix design (i.e. cement and water contents and presence of additives) and curing conditions (i.e. temperature, humidity, CO₂ concentration and duration). The initial studies presented in this report investigated the influence of these factors on the carbonation and mechanical performance of MgO cement concrete. The findings of this study improved the understanding of the carbonation mechanisms of MgO cement and provided a set of ideal mix designs and curing conditions that enhanced the performance of MgO cement concrete.

A subsequent study highlighted that temperature and CO₂ concentration influenced the formation and stability of HMC phases. To study the mechanical performance of MgO cement concrete under high temperatures, the stability and transformation of hydration and carbonation products were investigated under temperatures of 40-550 °C. Results showed that MgO cement-based concrete had good heat resistance until 350 °C. This study not only facilitated the understanding and controlling of the properties that affected the stability of the strength-providing phases, but also formed a pathway for the development of a range of MgO-based construction products relying on the sequestration of CO₂ for strength gain.

During their lifetime, concrete structures may suffer from deterioration due to various factors such as weathering, chemical attack and abrasion. The ability to resist these deterioration conditions is related to the durability of concrete. To study the mechanical performance and microstructural changes of carbonated MgO cement-based mixes under aggressive environments, concrete samples with different mix compositions were subjected to four types of chemical attack involving chloride and sulfate solutions, freeze thaw, and seawater environments. The results indicated the higher durability of MgO cement-based mixes when subjected to the aggressive environments in comparison of PC-based mixes was due to the lower solubility of the former. This was followed by a study of the feasibility of the scaled-up production of MgO-based construction blocks. A comparison of the performance of these commercial-sized samples with lab-scaled samples indicated the feasibility of using these binders on a large scale.

The combination of studies presented in this report clearly revealed the influence of key parameters such as concrete mix design and curing conditions on the performance and microstructural development of MgO-based concrete blocks, as well as the durability and the scaling-up feasibility of the developed formulations. Comparison of MgO-based blocks with corresponding PC-based blocks were provided in terms of performance and microstructural development. These findings not only facilitate understanding and controlling the properties affecting the performance and microstructure of MgO cement-based mixes, but also demonstrated the potential of using MgO cement-based concrete on a large scale in non-structural applications.

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Figure 7.2 Compressive strength of lab-scale samples and scaled-up samples

Figure 7.3 XRD pattern of scaled-up samples after (a) M40 (b) M20F20 (c) M20G20 (M: MgO, B: brucite, HM: hydromagnesite, HT: hydrotalcite, Mu: mullite, K: kaolinite, G: gypsum, C: calcite, P: portlandite, Mc: magnesite)

Figure 7.4 TGA curves of scaled-up and lab-scale samples (a) MgO samples (b) M20F20 samples (c) M20G20 samples

Figure 7.5 SEM images of scaled-up samples: (a) M40 1d (b) M40 28d (c) M20F20 1d (d) M20F20 28d (e) M20G20 1d (f) M20G20 28d

Figure 7.6 Commercial trial of MgO concrete blocks

Abbreviations

C-S-H	Calcium Silicate Hydrate
DTA	Derivative Thermogravimetric Analysis
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscopy
GGBS	Ground Granulated Blast-furnace Slag
HMCs	Hydrated Magnesium Carbonates
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
M-S-H	Magnesium Silicate Hydrate
PFA	Pulverized Fly Ash
PC	Portland Cement
PSD	Particle Size distribution
RH	Relative humidity
SC	Standard consistency
SCMs	Supplementary Cementitious Materials
TGA	Thermogravimetric Analysis
UCS	Unconfined Compressive Strength
XRD	X-ray Diffraction

Chapter 1 INTRODUCTION

This chapter introduces the research background and the necessity of this study. MgO cement as a novel binder is studied as a replacement for PC to reduce the environmental impacts of PC. The advantages of carbonated MgO cement comparing to PC are shown, and the significance of carbonation of MgO cement to achieve high mechanical performance is illustrated. The factors controlling carbonation are listed, and the main factors influencing the carbonation of concrete mixes are the diffusivity of CO₂ and its reactivity with concrete. This is followed by the aims of the research: enhance the carbonation of MgO cement and investigation the performance of MgO cement concrete in harsh environment. Five objectives presented in the thesis are listed, the methods used for analysis are also shown. Novelty of this research is highlighted, and the significance of the research is shown. The layout of this report is presented, totally eight chapters are included.

1.1. Research background

The increased concentration of greenhouse gases such as carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) due to human activity is the main cause of global warming, one of the biggest environmental challenges ever faced by humanity. The concentrations of these greenhouse gases, which were measured as 410 ppm in 2018 (Ng, Tasnim, & Co, 2018), exceeded the pre-industrial levels by around 40%. According to IPCC, each of the last three decades has been successively warmer at the Earth's surface than any preceding decade since 1850. Some of the visible impacts of climate change are the continuous warming of the atmosphere and ocean, increase in the concentrations of greenhouse gases, reduction in the amounts of snow and ice, and rise in sea levels (Stocker, 2013). In spite of all the recent advances on carbon management, global greenhouse gas emissions are still continuing to rise (Anderson, 2007). Global temperatures have increased about 0.8°C

during the last century, two-thirds of which took place after 1970, in line with the increase in human activities (Carnesale, 2011; Rifkin, 2008). About half of the glaciers in the European Alps disappeared from 1850 to 1980, which are still continuing to melt as of today. Sea levels are increasing at a rate of 0.8-3.0 mm/year, and are predicted to rise to 2.2-4.4 times of their present value ((Damtoft, Lukasik, Herfort, Sorrentino, & Gartner, 2008). These not only endanger the balance of natural ecosystems, but also threaten our food supplies and living environment (Houghton, 2009; Lu, Vecchi, & Reichler, 2007).

The cement industry plays a very important role in alleviating the effects of global warming within the built environment as the production and use of cement is a major contributor to CO₂ emissions. Due 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. Since its introduction in the 19th century, PC dominated the construction market with an ever rising product range (Aïtcin, 2000). Currently, more than 4 billion tons of PC is produced each year (USGS, 2017), resulting in the emissions of approximately 0.87 ton of CO₂ for every ton of PC produced, accounting for 5-7% of global anthropogenic CO₂ emissions (Anderson, 2007; Damtoft, Lukasik, Herfort, Sorrentino, & Gartner, 2008; Initiative, 2002; Quillin, 2008). Additionally, PC production involves the consumption of 1.5 tons of raw materials (Li, Ding, & Zhang, 2004), 1.2 tons of CaCO₃, and 120 kg of coal for every ton of PC clinker (Gartner, 2004; Quillin, 2008; Tsiliyannis, 2012). This process necessitates 10–11 EJ of annual energy consumption, which accounts for about 2-3% of global and 10-15% of total industrial energy use in the world (Juenger, Winnefeld, Provis, & Ideker, 2011; Tae, Baek, & Shin, 2011), most of which are non-renewable.

Innovations are continuously introduced in terms of materials with reduced energy and CO₂ emissions as replacements for PC (Damtoft 2008; Hasanbeigi, 2014; Initiative, 2002; Lothenbach, Scrivener, & Hooton, 2011; Shi, Jiménez, & Palomo, 2011). Reactive magnesium oxide (MgO) cements, a mixture of PC and reactive magnesia in different proportions depending on their intended application ranging from structural concrete to porous masonry units, have recently emerged as a promising alternative. For the last 40

years, MgO cements have been used in dam construction as an expansive additive to compensate PC shrinkage (Mo, Deng, & Tang, 2010). Recent lab-scale trials performed in different research institutions since 2001 have identified the carbonation potential of MgO, presenting it as an alternative for PC due to the high strengths gained when subjected to CO₂ curing (John & Harrison, 2002; Li, 2013; Liska, 2009; Unluer, 2012; Unluer & Abir Al-Tabbaa, 2011; Unluer & Al-Tabbaa, 2014; Vlasopoulos, 2012).

Some of the main technical and sustainability advantages of MgO cements over PC are listed below:

- (1) **Permanent sequestration of CO₂:** MgO cements can reabsorb the CO₂ emitted during their production and can gain strength through this carbonation process.
- (2) **Lower production temperatures:** The manufacturing temperature of MgO is much lower than that of PC (750 vs. 1450 °C), which enables MgO cement to enable a high reactivity and specific surface area.
- (3) **Ease of manufacturing:** MgO cements can be manufactured in existing PC production plants without need for alterations. This highlights the feasibility of producing MgO cements on a large scale.
- (4) **Improved mechanical performance and durability:** MgO cements can achieve higher strengths than corresponding PC mixes when subjected to CO₂ curing. They also indicate improved durability against acid attack due to the dense structure of MgO concrete and low solubility of its phases.
- (5) **Ability to combine with waste materials:** MgO cements have the capability of combining with other waste materials such as ground granulated blastfurnace slag (GGBS) and fly ash without much reduction in strength as the addition of waste materials does not influence the formation of carbonation products in MgO cements. The incorporation of high proportions of waste materials in MgO cements can increase the sustainability and bring down the overall cost of the final product.

Understanding the factors that influence the carbonation process of MgO cement-based concrete mixes is necessary to increase the degree and rate of carbonation (Bary & Sellier, 2004a; Hyvert, Sellier, Duprat, Rougeau, & Francisco, 2010; Park, 2008; Van Balen, 2005).

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) (Jin, Gu, Abdollahzadeh, & Al-Tabbaa, 2013; Jin, Gu, & Al-Tabbaa, 2015; Martin Liska & Abir Al-Tabbaa, 2009; C Unluer & A Al-Tabbaa, 2012), (ii) curing conditions (curing time, CO₂ concentration and pressure, relative humidity (RH), temperature and wet/dry cycling frequency) (L. Mo & Panesar, 2012; C Unluer & Al-Tabbaa, 2014), and (iii) presence of additives (SCMs, admixtures, cement and aggregate replacements) ((Panesar & Mo, 2013; Unluer & Al-Tabbaa, 2013; Unluer & Al-Tabbaa, 2015; L. Vandeperre, Liska & Al-Tabbaa, 2008b; Yi, Liska & Al-Tabbaa, 2013). Figure 1.1 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.

Figure 1.1 Factors controlling concrete carbonation

Previous studies on carbonated MgO formulations have reported its hydration and carbonation mechanisms (Dung & Unluer, 2016, 2017b; Liska & Al-Tabbaa, 2009; M Liska, Vandeperre & Al-Tabbaa, 2006) and have attempted to improve these via the use of different mix designs (Liska & Al-Tabbaa, 2009; Mo & Panesar, 2012; Ruan & Unluer, 2017a), additives (Liska 2006; Ruan & Unluer, 2017b; Unluer & Al-Tabbaa, 2015) and curing conditions (Liska, Vandeperre & Al-Tabbaa, 2008; Unluer & Al-Tabbaa, 2014; Vandeperre & Al-Tabbaa, 2007). Studies performed on the use of reactive MgO as a binder in concrete mixes have shown its capacity to fully carbonate under accelerated carbonation conditions, during which the CO₂ concentration is raised from ambient (0.04%) to accelerated (5-20%) levels to increase the rate of the carbonation reaction (Unluer & Al-Tabbaa, 2013, 2014). Since the carbonation process relies on the supply of CO₂, an obvious improvement in density, strength and stiffness can be achieved by curing MgO samples under relatively high CO₂ concentrations (e.g. 5-20%) (Liska & Al-Tabbaa, 2009; Unluer & Al-Tabbaa, 2014). The mix designs proposed in these studies can be utilized in the sequestration of CO₂ obtained from flue gases emitted by power plants, meanwhile resulting in a notable strength development.

The research presented in this report studied the key factors that influence the mechanical performance and microstructure development through the hydration and carbonation processes of MgO. A series of comprehensive investigations including mix design (i.e. cement types, cement and water contents), introduction of supplementary cementitious materials (i.e. PFA and GGBS) and curing conditions (i.e. temperature, relative humidity and CO₂ concentration) were performed initially to establish an understanding of the ideal mix design and curing conditions. Further studies investigated the stability of the formed hydration and carbonation products in MgO cement concrete, which involved aggressive conditions such as high temperature environments and chemical attacks. Finally, the use of MgO as a binder in scaled-up concrete blocks was investigated to evaluate the feasibility of commercializing MgO cement-based concrete.

1.2. Aims, objectives and novelty of the research

The aim of the work presented in this thesis is to (i) enhance the carbonation, mechanical performance and microstructural development of MgO cement concrete containing different additives, (ii) evaluate the stability of the formed phases under various conditions involving high temperatures and aggressive environments, and (iii) provide a comparison between commercial and lab scale blocks in terms of performance and microstructure, via a detailed experimental analysis involving various conventional and novel approaches.

The objectives and the approach followed in this research can be divided into five main areas:

1. Investigation of the influence of mix composition (i.e. cement type and cement and water contents) and curing conditions (i.e. temperature, relative humidity and CO₂ concentration) on the hydration, carbonation and mechanical performance of MgO cement blocks. This part commences with the analysis of the performance of MgO cement-based concrete in comparison with PC-based concrete under natural and accelerated curing conditions.
2. Investigation of the effect of pre-conditioning involving the use of elevated temperatures and humidity on the reaction mechanisms, mechanical performance and microstructural development of MgO cement-based formulations.
3. Investigation of the influence of high temperature environments on the formation, stability and transformation of hydrated magnesium carbonates (HMCs). This study involved subjecting MgO-based concrete blocks to different temperatures ranging between 40 and 550 °C, after which the chemical and physical analysis of the transformation of HMCs were conducted.
4. Investigation of the mechanical performance and stability of the hydration and carbonation products in MgO cement concrete in comparison to PC-based concrete under aggressive conditions for up to 6 months.

5. Investigation of the feasibility of producing MgO-based blocks with various compositions on a larger scale through commercial trials. This study involved a detailed comparison of the scaled-up MgO cement blocks with lab-scale samples.

All the research presented in this thesis involved the analysis of the mechanical performance and reaction mechanisms of the prepared formulations via porosity, pH, isothermal calorimetry and compressive strength measurements at different durations and conditions. The formation of different phases within MgO cement concrete was investigated via X-ray diffraction (XRD), thermogravimetric/derivative thermogravimetric (TG/DTG) and scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) analyses. This study also involved the use of the quantitative analysis of the hydration and carbonation products in MgO cement via TGA and XRD. This comprehensive investigation of the main factors influencing the mechanical and microstructural development of MgO formulations have enabled the development of a better understanding about the carbonation capacity of MgO cement concrete and formed a pathway for the development of a range of MgO-based construction products relying on the sequestration of CO₂ for strength gain.

Furthermore, this research focused on two novel research areas that have not been investigated in detail until now. The first research area involved the stability of phases in carbonated MgO cement-based concrete under high temperatures. Previous studies have reported the effects of temperature and CO₂ concentration on the formation, stability and transformation of various Mg-carbonates, albeit not in the cement context. Although the performance of carbonated MgO-based samples is dependent on the formation and stability of carbonation products, the changes in the properties of phases under different conditions and their effect on the overall sample performance have not been studied in detail until now. The second research area presented the durability of MgO cement concrete under various aggressive environments. Until now, very limited information on the performance of MgO cement concrete under various durability conditions such as chloride and sulfate attack, freeze-thaw cycling and seawater exposure has been reported. Accordingly, the

findings reported in this study present new information on the use of MgO-based formulations and are therefore novel.

1.3 Layout of the thesis

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 research topics investigated in this study and presents their main goals and objectives.

Chapter 2 provides a detailed literature review on the production and classification of MgO cement, and its applications, especially within concrete blocks. The hydration and carbonation processes of MgO cement and the factors influencing these reactions are presented. The usage of supplementary cementitious materials in concrete was discussed. A section about the stability of carbonation products under high temperatures and the durability issues concerning concrete samples was included.

Chapter 3 presents information on the materials, sample preparation and curing methods and experimental methodology used in this report.

Chapter 4 presents and discusses the influence of mix design, curing conditions and pre-conditioning on the performance and reaction mechanisms of MgO cement-based formulations in comparison to those involving PC.

Chapter 5 presents and discusses the results obtained from the high temperature exposure of MgO cement-based formulations and the stability of carbonate phases under these conditions.

Chapter 6 presents and discusses the performance of MgO-based concrete involving the use of various SCMs under different durability conditions and provides a comparison with PC-based concrete in terms of mechanical performance and microstructural changes.

Chapter 7 presents and discusses the difference between scaled-up MgO cement concrete blocks and lab-scale samples via a detailed comparison considering strength development and carbonation degree.

Chapter 8 highlights the main findings of each study and presents a guideline for further studies to be performed in this area.

2. LITERATURE REVIEW

This chapter presents the usage of MgO as cement binder in the past decades, and different applications of MgO cement are listed. Two major routes for production of MgO cement are presented, and the environmental impacts of production of MgO cement is compared with that of PC. Application of MgO with different grades are listed. Some advantages of carbon capture via usages of MgO cement are highlighted. The mechanism of hydration and carbonation processes of PC and MgO are presented, and the significance of hydrated magnesium carbonates (HMCs), the carbonation products of MgO cement, is presented. Influence of different factors including mix design and curing conditions on hydration and carbonation of PC and MgO cement are mentioned. Effects of cement replacement with pulverized fly ash and ground granulated blast-furnace slag are explicated. The stability and transformation of hydration and carbonation products of PC and MgO cement under high temperature and chemical attacks are presented. This is followed by a review of the previous studies on MgO cement-based concrete blocks.

2.1 MgO cements

2.1.1 History and applications of MgO cements

MgO has been used in different parts of the construction industry for thousands of years. It was used as a mortar component and stabilizer for soil bricks in the Great Wall of China in the 7th century BC and as a building material in the Terracotta Army in the 3rd century BC (Concreate, 2013). For the last 40 years, MgO cements have been used in dam construction as an expansive additive to compensate PC shrinkage (Mo, 2010). Recent lab-scale trials performed in different research institutions since 2001 have identified the

carbonation potential of MgO, presenting it as an alternative for PC due to the high strengths gained when subjected to CO₂ curing (Harrison, 2002; Li, 2013; Liska, 2009; Unluer, 2012; Unluer & Al-Tabbaa, 2011; Unluer & Al-Tabbaa, 2014; Vlasopoulos, 2012).

Other binders that make use of MgO in their compositions include magnesium oxychloride (MOC), magnesium oxysulfate (MOS), and magnesium phosphate (MAP) cements. MOC cements are highly fire and mold resistant and can be easily applied on different surfaces. They are used to replace traditional gypsum drywalls wall and ceiling covers (Deng, 2003; Shand, 2006). MOS cements can enhance the performance of concrete in high temperature conditions and are applied in nuclear applications (Beaudoin & Feldman, 1977; Beaudoin & Ramachandran, 1978). MAP cements contain low reactivity MgO such as hard-burned and dead-burned MgO instead of reactive MgO to avoid the rapid reaction between a highly reactive MgO and phosphate salts. They present a good water resistance and high early strengths, and are used in industrial flooring, fire protection, insulating panels and rapid repair applications (Buj, Torras, Rovira & de Pablo, 2010; Otto, 2012; Soudée & Péra, 2002).

2.1.2 Production of MgO cements

MgO can be produced by two major routes: (i) Calcination of magnesium carbonate (magnesite, MgCO₃) as shown in Equation 2.1, and (ii) synthesis from brine or seawater. MgCO₃ can be found in natural deposits with purity levels of about 90-95% around the world. Magnesite usually exists in veins, ultramafic rocks, serpentine and other magnesium rich rocks. It is estimated that about 14 million tonnes/year of MgO is produced worldwide. For comparison, production of PC exceeds 4 billion tonnes/year (USGS, 2017). The 3.7 billion tonnes of magnesite reserves in China account for ~29% of the world's total reserves (Li, Zhang, Shao & Zhang, 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, 2013) and the leading producers are China,

Russia, and Turkey, who are responsible for 49%, 12%, and 6% of total MgO production, respectively (Palomo, Grutzeck, & Blanco, 1999). 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. China has the largest magnesite reserves in the world and is the largest producer, consumer and exporter of MgO. Export taxes imposed on MgO products by the Chinese government in 2008 increased costs, incentivizing competing countries to increase local MgO production capacities rather than relying on low cost imports from China (IHS, 2014). The current cost of reactive MgO is ~\$339/tonne, which is higher than PC (~\$79/tonne) (Liska, Al-Tabbaa, Carter & Fifield, 2012a; Liska, Al-Tabbaa, Fifield & Carter, 2012).

During the decomposition of 1 ton of magnesite, theoretically 0.48 tons of MgO and 0.52 tons of CO₂ are emitted. This corresponds to 1.08 tons of CO₂ / ton of MgO. If the CO₂ emitted from fossil fuel burning (0.328 tons / ton of MgO) is also included in this calculation, the total amount of CO₂ emitted during the production of 1 ton of MgO can be reported as ~1.4 tons. The two steps considered for the total energy requirement during this process are the: (i) heating of magnesite from ambient temperature to required temperature to enable decomposition, and (ii) decomposition of magnesite into MgO. The energy consumption for these two processes is reported as 1131 kJ/kg of MgO and 1284 kJ/kg of MgO, respectively (Liska & Al-Tabbaa, 2009). This corresponds to a total energy requirement of 2415 MJ/ton of MgO. Table 2.1 presents a comparison of MgO and PC production in terms of CO₂ emissions, energy consumption and raw material requirements.

Table 2.1 Environmental impacts of MgO cement and PC production (Liska & Al-Tabbaa, 2009)

Parameter	MgO	PC
Total energy requirement (MJ/t)	2415	1760
Raw material required (t/t)	2.08	1.5
Carbon dioxide emissions (t/t)	1.4	0.85
Desirable carbonation rate	100%	Up to 30%
Final emissions after carbonation (t/t)	0.22	0.37

Although the CO₂ emissions and energy consumption of MgO production is higher than that of PC, MgO cements have the ability to improve the mechanical performance of mixes by sequestering the CO₂ emitted during their production through the carbonation process.

Mg is the third most abundant element in seawater, while brine wells and lakes also provide a large amount of magnesium salt solutions. Because of its higher concentrations of the magnesium ion (9%), brine is a better source of magnesium than seawater. To obtain 1 kg of MgO, 25 liter of brine or 568 liter of seawater is needed (Marietta, 2009). The chemical reaction showing synthesis MgO from brine is presented in Equations 2.2 and 2.3. During this process, dolomitic limestone (dolime) is used to provide the necessary Ca(OH)₂ to increase the pH of the solution to 10.5 so that Mg(OH)₂ can precipitate. The obtained Mg(OH)₂ is heated to 350°C to produce MgO, resulting in a total energy consumption of 6700 MJ/tonne of MgO (Shand, 2006).

2.1.3 Classification of MgO cements

MgO is categorized under 4 different grades according to its reactivity (Jin & Al-Tabbaa, 2013a; Shand, 2006), which is mainly determined by the calcination conditions (temperature and duration) used during its production. Light-burned (i.e. reactive or caustic) MgO is calcined at 700-1000°C and has very high specific surface area (SSA) and reactivity. The properties and applications of light-burned MgO have been reported in several studies (Birchal, 2001; Caraballo, Roetting, Macias, Nieto & Ayora, 2009; Chau & Li, 2008; Fukumoto, Sasaki, Moriyama & Hirajima, 2011; Garcia, 2004; Jensen, Aaes & Madsen, 1986; Jin & Al-Tabbaa, 2014; Rotting, Cama, Ayora, Cortina & De Pablo, 2006; Unluer & Al-Tabbaa, 2014), including its use in cementitious materials (Liska & Al-Tabbaa, 2009; Mo & Panesar, 2012; Unluer & Al-Tabbaa, 2011; Vandeperre 2008b; Vandeperre & Al-Tabbaa, 2007; Vandeperre, Liska & Al-Tabbaa, 2007). Hard-burned MgO is calcined at 1000-1400°C and has relatively low SSA and reactivity. It is typically used in applications that exploit the expansion properties of MgO (Gao, 2008; Liwu Mo, Deng, Tang & Al-Tabbaa, 2014). Dead-burned MgO (periclase) is calcined at 1400-2000°C, has low SSA and is unreactive (Wagh, 2004). It is mainly used in refractories (Ahari, Sharp & Lee, 2002; Silva, Aneziris & Brito, 2011), the major use of MgO. Fused MgO, which possesses low hydration energy, high thermal shock resistance, and a compact structure, is used in monolithic refractories and electrical insulating (Canterford, 1985; Li 2015).

In general, higher calcination temperatures decrease the reactivity and SSA and increase the crystallinity and density of the final MgO powder. Current applications for reactive MgO include its use as a sorbent in pollution abatement (Caraballo, Rötting, Macías, Nieto, & Ayora, 2009; Harrison, 2001), animal feed supplement (Jensen, Aaes & Madsen, 1986), filtering agent (Aneziris, 2013), and construction material (Liska & Al-Tabbaa, 2008). Reactive MgO can be mixed with PC, slag, and fly ash in different proportions to form different binders with a variety of uses.

2.1.4 Carbon capture and storage

Carbon capture and storage (CCS) is regarded as a method with a high potential to reduce the total concentration of CO₂ in the atmosphere. Geological sequestration of CO₂, whose basic principle is to compress CO₂ in mineral form and store it permanently via chemical or physical processes, is currently being investigated on a global scale in terms of its technical and economic feasibility by different parties involved in the cement industry, such as the European Cement Research Academy (ECRA) (Electronic Commerce Research and Applications (ECRA), 2012). MgO cements have the potential to sequester CO₂ in construction products and present several advantages, as listed below:

1. MgO is present in large amounts and high concentrations in most regions of the earth's crust. It is the 7th most abundant mineral on earth, and 3rd in seawater. It can be used as a CO₂ adsorbent on an industrial scale (Chaka & Felmy, 2014; Huijgen & Comans, 2003).
2. The carbonation products of MgO are stable in the long-term at elevated temperatures, enabling stable storage of CO₂ (Ballirano, De Vito, Ferrini & Mignardi, 2010b; Ballirano, De Vito, Mignardi & Ferrini, 2013).
3. The dehydroxylation process experienced at higher temperatures can reconstruct the surface of previously formed carbonation products, producing high reactivity products, which improves carbonation capacity (Béarat, McKelvy, Chizmeshya, Sharma & Carpenter, 2002).

2.2 Hydration of PC and MgO

2.2.1 Hydration of PC

Hydration of PC is a complex process that leads to strength gain. Alite (C₃S), belite (C₂S), aluminates (C₃A) and a ferrite (C₄AF) are the main phases in PC which hydrate at different

rates based on their chemical properties. During the hydration of alite, which determines the setting and hardening of PC, two types of calcium silicate hydrate (C-S-H) with a CaO/SiO₂ molar ratio between 1.4 and 2.0 form along with calcium hydroxide (Ca(OH)₂). The chemical reaction showing the hydration of alite is shown in Equation 2.4.

The hydration of belite (C₂S) is similar to that of alite, forming C-S-H with a CaO/SiO₂ ratio of 1.1-1.6. Tricalcium aluminate (C₃A) reacts with calcium sulphate during its hydration, which takes place much faster in the absence of calcium sulphate. Gypsum (CaSO₄·2H₂O) is added to PC to prevent fast hydration of C₃A, which will cause flash set. The initial hydration product is calcium sulfoaluminate (ettringite, Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O). If the gypsum reacts completely before the C₃A, ettringite formed previously will react with C₃A to form monosulfoaluminate. These two stages of hydration of C₃A is presented in Equations 2.5 and 2.6. The hydration products of calcium aluminoferrite (C₄AF) are similar to those of C₃A, potentially taking place at a faster rate.

The scanning electron microscopy (SEM) images of the major hydration products of PC are shown in Figure 2.1. The plate-like hexagonal crystals of Ca(OH)₂ can be compared with the needle-like crystals of ettringite shown in Figure 2.1(a). The microstructure of C-S-H indicates irregular particles with rough surfaces as shown in Figure 2.1(b).

Figure 2.1 SEM images of the hydration product of PC: (a) $\text{Ca}(\text{OH})_2$ and ettringite, (b) $\text{Ca}(\text{OH})_2$ and C-S-H (Franus, Panek, & Wdowin, 2015)

2.2.2 Hydration of MgO

The major hydration product of MgO cements is brucite ($\text{Mg}(\text{OH})_2$). Another hydration product hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}(\text{H}_2\text{O})_4$) can be observed in ambient condition (Vandeperre, Liska & Al-Tabbaa, 2007). Unlike PC hydration, the formation of brucite does not contribute to strength development by itself and can cause volume expansions which lead to cracks, depending on the reactivity of the MgO used. The occurrence of these expansions can be avoided if reactive MgO is used as opposed to hard- or dead-burnt MgOs. Hydration of reactive MgO completes at an early age compatible with PC, eliminating any late expansion problems (Vandeperre 2008b). The process of hydration is expressed in Equation 2.7.

The hydration mechanism of MgO follows these steps: (i) adsorption of water at the surface and its simultaneous diffusion inside porous MgO particles, (ii) dissolution of oxide within these particles, changing porosity with time, and (iii) creation of supersaturation, nucleation and growth of brucite at the surface of MgO (Rocha, Mansur & Ciminelli, 2004). During this process, a layer of newly formed brucite forms on the surface of MgO,

imposing an additional resistance that limits the further continuation of the hydration process. In the case of applications involving MgO cements, this mechanism presents a constraint on the progress of hydration and the subsequent carbonation process, which hinders strength development. This is one of the main challenges faced by MgO-based binders that rely on carbonation for hardening. Therefore, understanding the dissolution and hydration kinetics of MgO plays a critical role in determining the mechanical performance of these binders. As the hydration of MgO takes place after the supersaturation of brucite, followed by its precipitation on the MgO surface, the reaction rate is controlled by proton attack or desorption of Mg^{2+} and OH^- ions. The rate controlling factor depends on the pH interval and is identified as the Mg^{2+} concentration, diffusion and adsorption of OH^- ions when the pH is <5 , ~ 5 , and >7 , respectively (Fruhworth, Herzog, Hollerer & Rachetti, 1985).

Other factors that affect the progress and kinetics of the hydration of MgO cements include the phase composition of the binder, particle size distribution and SSA of cement particles, reactivity of MgO, water content, curing temperature and inclusion of additives (Birchal, Rocha, Mansur & Ciminelli, 2001; Rocha, Mansur & Ciminelli, 2004). The morphology of brucite can vary depending on the curing conditions and mix design, as can be seen from the SEM images shown in Figure 2.2.

Figure 2.2 SEM image of brucite at different pH values and temperatures (Yan, Xue, Zou, Yan, & Wang, 2005)

2.3 Carbonation of PC and MgO

2.3.1 Carbonation of PC

The carbonation of PC can be described as chemical reaction between the CO_2 present in air and the calcium contained in the pore solution of concrete, in equilibrium with the hydration products of cement (Bary & Sellier, 2004b). There are two stages in PC carbonation. During the first step CO_2 dissolves in water to form carbonic acid, which then reacts with $\text{Ca}(\text{OH})_2$ and C-S-H to form calcite (CaCO_3) as shown in Equations 2.8-2.10.

During the carbonation of PC, C-S-H, which is the main source of strength, is converted into CaCO_3 and a highly porous and hydrous form of silica, resulting in strength loss. Therefore, carbonation is not a desirable reaction in terms of maintaining the mechanical performance and durability of PC mixes. The progress of carbonation can also result in the corrosion of steel reinforcement, which are covered by a thin passive oxide layer preventing the occurrence of corrosion at high pH values. Carbonation can decrease the pH value from 12.5 to a value below 9 by transforming the alkaline hydration products into other forms, which destroys the protective layer.

2.3.2 Carbonation of MgO

In the presence of sufficient water, brucite reacts with CO_2 , leading to the formation of hydrated magnesium carbonates (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 ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$) and artinite ($\text{Mg}_2\text{CO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$). The microstructures of these carbonates, which are the main sources of strength, are shown in Figure 2.3. The process of carbonation of MgO cement can be summarized with the reactions shown in Equations 2.11-2.14.

Figure 2.3 SEM images of HMCs: (a) nesquehonite (Ferrini 2009b), (b) dypingite (Power, Wilson, Thom, Dipple & Southam, 2007), (c) hydromagnesite (Teir 2007), (d) artinite (Romano, 2003)

Carbonation is a critical process for MgO cement binders as they harden and gain strength via the formation of HMCs. Strength development of MgO binders subjected to carbonation is related to: (i) the increase in density as carbonation reactions are expansive processes (i.e. the formation of HMCs causes significant expansion and increases the solid volume by a factor of 1.8-3.1) that reduce the overall pore volume; and (ii) microstructure evolution as the morphology and the binding strength of the carbonate crystals contribute to the network structure. Several studies have reported the importance of the morphology of carbonates, as opposed to their amount, in determining final performance. HMCs have microstructures with varying morphologies and add microstructural strength to 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 established by HMCs are more beneficial than rounded or tabular crystals because of the 3D structures formed. Nesquehonite is prismatic and forms star-like clusters, whereas dypingite and hydromagnesite are composed of rounded rosette-like crystals. The elongated morphology of nesquehonite reduces porosity and increases stiffness, raising the solid volume by a factor of 2.34 upon its conversion from brucite. The compact and interlocked network-like structure established by interconnected and well developed crystals controls the overall performance (De Silva, Bucea, Moorehead, & Sirivivatnanon, 2006). This is further supported by the bulk “micro-aggregate” formed through localized carbonation, which also contributes to the creation of a dense matrix compared to PC pastes (Mo & Panesar, 2012).

The formation of HMCs in carbonated MgO systems depends on the reactivity and impurities present within MgO, along with the temperature and the CO₂ concentration to which they are exposed. 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 transformation pathway of HMCs under different curing conditions and its effect on the overall performance of MgO cement binders is currently under investigation. This plays a significant role in comprehending the stability and determining suitable end products employing MgO cements in the long term.

2.4 Factors influencing the degree and rate of carbonation

Three main factors controlling the rate and degree of carbonation as well as the associated strength development are: (i) Mix composition (cement and aggregate components, w/c ratio, particle packing arrangement of different aggregate profiles) (Jin & Gu 2013; Jin 2015; Liska & Al-Tabbaa, 2009; Unluer & Al-Tabbaa, 2012), (ii) curing conditions (curing time, CO₂ concentration, relative humidity, temperature, wet/dry cycling frequency) (Mo

& Panesar, 2012; Unluer & Al-Tabbaa, 2014), and (iii) introduction of additives (waste materials, admixtures, cement and aggregate replacements) (Panesar & Mo, 2013; Unluer & Al-Tabbaa, 2013; Vandeperre 2008b; Yi 2013).

The progress of carbonation in cement mixes is related to the diffusivity and reactivity of CO₂ with the cement matrix. The former is decided by curing conditions and porosity of the overall concrete, whereas the latter is affected by the composition of the concrete. Since the carbonation process involves the diffusion of CO₂ into the cement matrix and its reaction with hydration products, it is important to understand the kinetics of this process in order to optimize carbonation and enhance the formation of HMCs and the overall sustainability of the concrete mixes prepared under this study. To enable this, the influence of each of these factors on the carbonation process is reported separately in subsequent sections.

2.4.1 Influence of pore system of hardened concrete on carbonation

The distribution of pores, overall porosity, and their interconnectivity, which influence the ease of CO₂ penetration into the cement matrix, are some of the main factors controlling the extent of carbonation. Previous studies on concrete carbonation have reported the influence of mix porosity on the extent of carbonation, and hence the mechanical performance and durability of concrete.

For cements, there are mainly two types of pores, gel pores and capillary pores. The size of capillary pores is 10 nm to 10 mm. Capillary pores exist in voids between cement particles and the pores are partially filled with free water. Gel pores, which present in the hydration products, have a larger size range from 0.5 nm to 10 nm, and constitute the internal porosity of the C-S-H gel phase. The pore system of concrete is shown in Figure 2.4. Both capillary pores and gel pores facilitates the transportation of CO₂. The sum of pores is controlled by the porosity of the concrete as well as hydration and carbonation

degree. A larger amount of large capillary pores forms in carbonation while capillary porosity stays the same.

Figure 2.4 Pore system in concrete (Powers & Helmuth, 1953)

Figure 2.5 Comparison of porosity between carbonated concrete and uncarbonated concrete (Ishida & Maekawa, 2000)

For traditional PC mixes, the ingress of CO_2 and other chemicals such as chloride through the existing pore system determines the durability and service life of concrete (Bramshuber, 2008). Earlier studies investigated the change of porosity of PC during carbonation and found that total porosity decreases in carbonation, which is due to the expansion of hydrates in concrete (Ishida & Maekawa, 2000). In these mixes, the transformation of $\text{Ca}(\text{OH})_2$ to form CaCO_3 leads to a decrease in porosity of concrete (Frías & Goñi, 2013; Johannesson & Utgenannt, 2001; Ngala & Page, 1997; Song & Kwon, 2007),

shown in Figure 2.5. The porosity as well as permeability of all samples decreased after carbonation, slowing down the ingress of further CO_2 within the samples.

Permeability is the direct indicator of CO_2 diffusion and it is determined by porosity of the concrete. Since it is easier to allow penetration of CO_2 in larger pores, capillary pores have more impacts on permeability than gel pores. Permeability is proportional to porosity, shown in Figure 2.6. However, permeability is only related to the porosity but also to the connectivity of the pores. The permeability of the concrete is controlled by large pores if there are enough capillary pores, and is determined by gel pores when the capillary pores were disconnected (Holly, Hampton & Thomas, 1993; Johannesson & Utgenannt, 2001; Luping & Nilsson, 1992; Song & Kwon, 2007). When capillary porosity is lower than 0.2, the absorption of concrete clearly reduces, which means pores are less connected.

As MgO cement-based mixes rely on the carbonation reaction for strength gain, an ideal mixture 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 blocks were chosen to be made in the study because contains coarse aggregates and is more porous than cement paste, which is favor for carbonation process.

Figure 2.6 Permeability vs. porosity in PC paste (Powers, 1958)

2.4.2 Influence of cement type and content on carbonation

Different types of cement have different mechanisms of hydration and carbonation, which significantly influence the mechanical properties. As discussed in previous section, Portland cement strength gain mainly depends on formation of C-S-H during hydration process and strength goes down when carbonation takes place. At the early stage of carbonation of PC, strength does not go down compared to non-carbonated PC as the degree of polymerization of the C-S-H is not affected by carbonation yet (Junior, Toledo Filho, Fairbairn & Dweck, 2015). Micro-cracks form in carbonation areas when deviatoric stress is present afterwards, which increase the permeability and decrease the strength of concrete (Fabbri 2009; Rimmelé, Barlet-Gouédard, Porcherie, Goffé & Brunet, 2008). On the other hand, the carbonation process is preferred for MgO cement, since the formation of H-M-Cs is the main source of strength.

The replacement of PC by MgO under natural curing results in reduced strengths due to the hydration of high content of MgO cannot provide sufficient strength (Liska & Al-Tabbaa, 2009; Vandeperre, Liska & Al-Tabbaa, 2006). When curing in accelerated carbonation condition, the conversion of brucite into nesquehonite under increased CO₂ concentrations led to an increase in density, stiffness, and toughness (Vandeperre & Al-Tabbaa, 2007).

Additives also effect porosity and thus carbonation. With addition of fly ash, larger pores can be found in carbonated concrete, which enhance the carbonation of PC (Frías & Goñi, 2013; Hill & Sharp, 2002; Ngala & Page, 1997). The carbonation rate of concrete with 21% pozzolan content (activated paper sludge + fly ash) was 2.2 times faster than PC due to porous structure which is good for diffusion of CO₂ and the pozzolanic reaction (Frías & Goñi, 2013). Lower replacement of silica fume (5, 10%) led to slower carbonation rate (Sulapha, Wong, Wee & Swaddiwudhipong, 2003). When the silica fume content increased to 30%, the carbonation degree of pozzolan concrete with lower w/b ratio improved as well as strength, compared with PC (Shi, Xu & Zhou, 2009). Lower strength and poor durability can be found in concrete with addition of fly ash, and adding ground blast furnace slag with

enough water supply can solve this problem (Johannesson & Utgenannt, 2001, Baoju, Youjun, Shiqiong & Jian, 2001; Liu, Xie, & Li, 2005; Ngala & Page, 1997).

2.4.3 Influence of aggregate on carbonation

Aggregate also play an important role in carbonation of concrete. The strength of the cement aggregate bond is regarded as a limiting factor of strength of concrete and aggregate can influence durability of concrete because it is related to permeability (Amirjanov & Sobolev, 2008; Bentz, Garboczi, Haecker & Jensen, 1999; Celik, 2009; Maso, 1980; Scrivener & Nemat, 1996). Larger size aggregates increased the vacuum water absorption and air permeability while saturated aggregates decrease the vacuum water absorption and air permeability (Pereira, Castro-Gomes & de Oliveira, 2009; Thiery, Dangla, Belin, Habert & Roussel, 2013). More fine aggregate content decreased the permeability as tortuosity increased (Shane, Mason, Jennings, Garboczi & Bentz, 2000). Aggregate grading did not affect carbonation as much as size of aggregate did (Basheer, Basheer & Long, 2005). Recycled aggregate had an inconspicuous effect on carbonation process or strength of PC (Otsuki, Miyazato & Yodsudjai, 2003; Zhan, Poon & Shi, 2013).

Particle size distribution (PSD) of the mix constituents is related to strength, porosity, diffusivity, shrinkage and microstructure of concrete (Bentz 1999; Ghiasvand, Ramezaniapour & Ramezaniapour, 2014; Olhero & Ferreira, 2004; Sobolev & Amirjanov, 2007). PSD also influences carbonation by controlling the dissolution rate of Mg^{2+} and transport of CO_2 within concrete mixes. The relationship between the carbonation of MgO blocks and PSD of aggregates was studied by Unluer and Al-Tabbaa (Unluer & Al-Tabbaa, 2012). Incorporation of gap grading within the aggregate PSD enhanced carbonation and thereby the strength of mixes studied.

2.4.4 Influence of water content on carbonation

Water is added to concrete to obtain easy workability. As the standard consistency of MgO (0.63) is higher than that of PC (0.34) due to the presence of agglomerates, MgO cements require higher amounts of water to hydrate and achieve the same consistency as PC mixes (Vandeperre 2008b). For the same water content, the final porosity of MgO cement is lower than that of PC. MgO is less effective than PC at filling the large pores because brucite is a crystalline product. This can explain the reduced strength and stiffness at early age when replacing PC with large amount of MgO (Vandeperre, Liska & Al-Tabbaa, 2008a). In addition, water itself occupies some space in concrete, but is indispensable for formation of hydration products, which fill the void between aggregate particles and increase the density and strength of the concrete (Hover, 1998, 2011; Mehta & Monteiro, 2006).

Increasing the water to solids ratio was found to improve carbonation and increase porosity and decreases strength (CEMEX USA, 2013; Lo & Lee, 2002; Nyame & Illston, 1981; Shamsai, Peroti, Rahmani & Rahemi, 2012; Vandeperre 2006) (Figure 2.7). Cement paste reaches a higher carbonation degree in a high RH environment (97% RH), when nearly all the hydration products were consumed. A thin layer of crystalline calcium carbonate formed outside silicate and hydroxide phases in a high humidity environment which prevents further carbonation (El-Turki, Ball & Allen, 2007; Ishida, Soltani & Maekawa, 2004). W/c ratio had an obvious influence on carbonation depth at early stage, but the depth difference between concrete with different w/c ratio diminished with time (Lo & Lee, 2002).

The effect of water and cement content on the carbonation of MgO cements has been analyzed. Lower w/c ratios resulted in higher initial strengths, whereas high w/c ratios favored carbonation in the longer periods. In the case of higher water contents, the pores were blocked by excess water, which hindered the penetration of CO₂ at early ages. However, this extra water proved to be useful at later ages for the continuation of hydration. Lower w/c ratios led to high initial strengths, followed by decreased long term strengths, explained by the insufficient formation of hydration products available for carbonation

(Unluer & Al-Tabbaa, 2011). For mixes containing 5% MgO and 90% PFA, decreasing water to solid ratio from 0.4 to 0.32 doubled the strength due to the denser microstructure (Vandeperre 2006).

Figure 2.7 Strength and porosity with different w/c ratios (Kim, Lee, Bang & Kwon, 2014)

2.4.5 Influence of hydration degree on carbonation

Hydration precedes the carbonation process, and the rate and degree of hydration will control the extent of carbonation. As hydration progresses, hydration products fill the available space between cement particles, which reduces capillary pores volume and the inter-connection of pores, decreasing permeability and hindering the diffusion of CO₂ further into the system (Ewertson & Petersson, 1993; Junior 2015; Liska & Al-Tabbaa, 2008; L. Mo & Panesar, 2012; Unluer & Al-Tabbaa, 2012). While a high initial porosity results in low strengths, a certain amount of porosity is needed for continuous carbonation.

The reactivity of magnesia can influence the hydration process of MgO cements, and therefore affect the carbonation and strength development of MgO cements. While MgO itself set faster than PC, the addition of MgO retarded the initial hydration of PC and

increased the setting time. This is because the formation of $\text{Mg}(\text{OH})_2$, which has smaller solubility than $\text{Ca}(\text{OH})_2$, reduced the $\text{Ca}(\text{OH})_2$ saturation ratio, and $\text{Mg}(\text{OH})_2$ formed on the surface of $\text{Ca}(\text{OH})_2$ hindering the further hydration of PC (Zheng, Xuehua & Mingshu, 1992). Retarding hydration may cause cracks in concrete (Hewlett, 2003).

Higher reactivity resulted in faster setting, which was beneficial to strength development at early ages but may decrease the workability of the mix (Chau & Li, 2008; Jin & Al-Tabbaa, 2013a). For high reactivity MgO cements, the hydration degree reached 70% within a day, attributed to the high special surface area of the highly reactive MgO (Jin & Al-Tabbaa, 2013b; Vandeperre 2007). But there is a hydration limit for MgO cements which means the hydration degree hardly increase after 28 days, and the unhydrated part of MgO cements attribute to the interior area of magnesia particle (Liu, Thomas, Ray & Guerbois, 2007).

In water curing, higher reactivity MgO increased strength of concrete while in air curing, higher reactivity led to more cracks due to higher capillary force in fine pores (Jin, Gu & Al-Tabbaa, 2014). Hydration of MgO causes the expansion of cement, and less reactive MgO cement has slower expansion at early stage but larger expansion later because the sintered MgO grains are taken apart by the expansion which increases reaction area (Mo 2010). Appropriate expansion is beneficial to the performance of mass concrete by avoiding thermal shrinkage (Mo 2014).

2.4.6 Influence of curing conditions on carbonation

Curing conditions including relative humidity, CO_2 concentration, and wet/dry cycling play a crucial role in the carbonation of cements.

As discussed earlier, the presence of excess water influences carbonation as it can slow down the transport of CO_2 (i.e. the diffusion rate of CO_2 is $16 \text{ mm}^2/\text{s}$ in air vs. $0.0016 \text{ mm}^2/\text{s}$ in water (CRC Press, 2010). However, water is required for the continuation of carbonation

reactions. Both excessively high and low RHs hinder the carbonation process (Galan, Andrade & Castellote, 2013; Liska 2008; Papadakis, Vayenas, & Fardis, 1991).

An obvious improvement in strength, density and stiffness can be achieved under high CO₂ concentration curing, especially when the w/c is high (Neville, 1997). This can be explained by the increase of solid volume with reducing porosity when brucite is converted into nesquehonite (Vandeperre & Al-Tabbaa, 2007). Carbonation needs ingress of CO₂ into the concrete pore system, and the CO₂ concentration outside concrete, which acts as the driving force, is one factor controls the carbonation rate. Carbonation depth increased with increasing CO₂ concentration, along with better mechanical performance and durability (Chi, Huang & Yang, 2002). In an accelerated carbonation test (5-20% CO₂ concentration), samples contain 10% and 20% MgO uptake similar CO₂ with PC after 56 days (Mo & Panesar, 2013). When CO₂ concentration reached 50%, the CO₂ intake capacity improved and there were more hydration products carbonated (Thiery 2013). Complete carbonation of the samples with denser microstructure and higher microhardness were observed in 99.9% CO₂ concentration, where magnesium calcite was formed, but nesquehonite only can be found in samples containing 40% reactive MgO (Mo & Panesar, 2012). Considering the kinetics of carbonations and factors influencing carbonation, analytical models can be used to get better understanding of the carbonation process (Bary & Sellier, 2004b; Hyvert 2010; Park, 2008; Van Balen, 2005).

Although the carbonation process can be accelerated in high CO₂, increasing the CO₂ concentration beyond 10% did not increase the amount of carbonation as other factors limited the diffusion of CO₂ within the samples beyond this point (Unluer & Al-Tabbaa, 2014). Subjecting the blocks to 5% CO₂ concentration resulted in strengths higher than 7 MPa after only 1 day of curing, which meets the strength requirement of commercial concrete blocks.

2.4.7 Influence of pre-conditioning (i.e. elevated temperature and humidity) on hydration and carbonation

Previous studies showed curing conditions such as temperature, relative humidity and duration of curing period play an important role in microstructural development and strength gain of PC. The hydration rate of PC increases when curing temperature increases up to 60 °C at early ages, and strength gain of concrete is accelerated as a result of elevated temperature. In general, chemical reaction rate doubles with an increase of 10 °C (Esmaily & Nuranian, 2012; Lin & Meyer, 2009; Wang, Li & Zhang, 2014). Elevated curing temperatures not only enhance the strength gain in the early stage but also help increase the chemical resistance of PC. More hydration products form during hydration process at higher temperature, which leads to a more heterogeneous distribution of the hydration products in the microstructure (Khatib & Mangat, 2002; Lothenbach, Winnefeld, Alder, Wieland & Lunk, 2007). A dense formation of C-S-H with a higher coarse porosity microstructure at higher temperature proved to be the reason for better chemical resistance to chloride and sulfate attacks in the early stage of exposure.

Although elevated curing temperature is proved to accelerate the initial hydration process, some negative effects of high temperature curing are found in later stages. Higher density of hydration products due to high temperature curing hinders the permeation of free water and thus slows down the hydration rate in the later age (Lin & Meyer, 2009; Wang, Miao, Feng & Yan, 2012). The rapid precipitation of hydration products leads to a non-uniform microstructure. The packing of C-S-H changes with different temperature, and the density of C-S-H increases from 2.03 kg/m³ to 2.27 kg/m³ when the temperature is raised from 20 °C to 60 °C. A lower strength and higher permeability of concrete was observed as the results of the coarser pore network with a more porous microstructure at later ages. Another reason for deleterious effects in the later stage is due to the delayed ettringite formation, which leads to expansion of concrete, when the temperature is higher than 70 °C (Escalante-Garcia & Sharp, 2001; Lothenbach 2007; Pichler, Schmid, Traxl & Lackner, 2017; Scrivener, Damidot & Famy, 1999). Previous studies revealed that more water is needed for concrete cured in elevated temperature to obtain the required workability, which

would bring down the long-term mechanical performance, especially considering the modulus of rupture, splitting tensile strength and flexural strength (Balendran & Martin-Buades, 2000). Partially replacing PC with supplementary cementitious materials (SCMs) such as fly ash or alkali-activated slag can reduce deleterious effects on strength development and chemical resistance of concrete in long-term (Bakharev, Sanjayan & Cheng, 1999; Khatib & Mangat, 2002; Maltais & Marchand, 1997). High temperature curing has more advantages on concrete with SCMs in favor of pure PC concrete considering the higher reaction activation energy of concrete with SCMs (Escalante-Garcia & Sharp, 2001).

Several techniques such as supercritical CO₂ and autoclave were introduced to the accelerate carbonation in concrete production (Knopf, Roy, Samrow & Dooley, 1999; Regnault, Lagneau & Schneider, 2009). Usually elevated temperatures (60-200 °C) enhance the strength development of concrete. This approach has high energy consumption and an alternative carbonation curing process with pre-conditioning was used in some studies to improve strength development.

In the pre-conditioning process, fan drying or oven drying was applied with relative humidity ranging from 50% to 98% and temperature ranging from 20 to 80 °C (Morshed & Shao, 2013; Shi, He & Wu, 2012; Shi & Wu, 2008; Zhan, Xuan, Poon & Shi, 2016). The results showed an increase in the permeability of concrete by eliminating water remains in the concrete pores. The carbonation degree of samples subjected to pre-conditioning was higher and a faster strength development was observed with a shorter curing duration when compared to steam curing. Temperature and humidity have a more significant effect on carbonation compared to pre-conditioning duration. However, humidity and temperature have potential negative impact on carbonation of PC. Although increasing temperature can accelerate carbonation process, the high temperature reduced the solubility of CO₂ (Vorholz, Harismiadis, Rumpf, Panagiotopoulos & Maurer, 2000), resulting in a higher pH in the pore water which led to a lower dissolution rate of calcium ions. High humidity can increase hydration rate but may hinder the CO₂ penetration. The

rate of moisture evaporation of concrete specimens during the pre-conditioning period has to be controlled. Fast moisture loss may result in specimen cracking.

2.5 Use of pulverized fly ash (PFA) and ground granulated blast-furnace slag (GGBS)

PFA and GGBS are widely used as SCMs in concrete mixes. Previous studies (Hemalatha & Ramaswamy, 2017; Kumar 2008; Özbay, Erdemir & Durmuş, 2016; Thomas & Bamforth, 1999) have shown that the inclusion of these materials can improve the performance characteristics of concrete due to their hydraulic or pozzolanic activity and the reduction in porosity due to their filler effect (Elahi, Basheer, Nanukuttan & Khan, 2010; Meyer, 2009). The use of PFA can minimize drying shrinkage and enhance the resistance of concrete to chemical attacks by decreasing the permeability of concrete. The formation of hydrate phases such as C-S-H, M-S-H and hydrotalcite, as well as the filler effect of PFA can increase the density and therefore improve the durability of PC-based concrete (Lammertijn & De Belie, 2008; Nath & Sarker, 2011; Roy, Arjunan, & Silsbee, 2001). Alternatively, concrete with high volumes of PFA has lower strength and durability than PC at early ages due to its slow rate of hydration (Langley, Carette, & Malhotra, 1992; Malhotra, Zhang, Read & Ryell, 2000). Other than PC mixes, the use of PFA in carbonated MgO-based mixes was shown to result in the formation of HMCs and magnesium calcite (Mg-CaCO_3), which improved the morphology and facilitated carbonate agglomeration, leading to dense and interconnected microstructures (Mo, Zhang, Panesar & Deng, 2017). MgO-PFA concrete cured in high concentrations of CO_2 demonstrated a rapid strength development and lower CO_2 emissions when compared to PC-based concrete (Mo, Zhang & Deng, 2015; Mo, Zhang, Deng & Panesar, 2016).

When included in PC mixes, GGBS, a by-product of the steel industry, can lead to the formation of C-S-H, along with C-A-S-H and hydrotalcite, depending on the mix composition. Previous studies showed that the use of GGBS can lead to lower permeability and greater resistance to chloride penetration, sulfate attack or freeze-thaw than PC-based concrete because of the limited formation of certain phases (e.g. ettringite) and denser

microstructures enabled via the formation of C-S-H (Escalante-Garcia, Espinoza-Perez, Gorokhovskiy & Gomez-Zamorano, 2009; Fu, Cai & Yonggen, 2011). In MgO-GGBS systems, the formation of hydrotalcite reduces the pore volume and increases strength. Brucite can be absent due to the consumption of the Mg^{2+} and OH^- during the hydration of GGBS (Haha, Lothenbach, Le Saout & Winnefeld, 2011). PC-MgO and PC-MgO-GGBS mortars subjected to high concentrations (99.9%) of CO_2 for up to 56 days were reported to achieve higher strengths than samples that were cured under ambient conditions due to the formation of calcite and magnesium calcite (Panesar & Mo, 2013). The presence of GGBS within these mixes improved strength development through the increased diffusion of CO_2 via the increased porosity and the formation of pozzolanic reaction products in uncarbonated zones.

2.6 Influence of temperature on the formation, stability and transformation of HMCs

Theoretically, the formation and stability patterns of the most commonly observed HMCs follow the transformation pathway shown in Equation 2.15. An increase in temperature can lead to the transformation of carbonates into those that are less hydrated, whereas a change in the CO_2 concentration can also result in the formation of different phases (Xiong & Lord, 2008).

Previous studies (Botha & Strydom, 2001; Fernández, Chimenos, Segarra, Fernández & Espiell, 2000; Hänchen, Prigiobbe, Baciocchi & Mazzotti, 2008; Hopkinson, Kristova, Rutt & Cressey, 2012; Königsberger, Königsberger & Gamsjäger, 1999; Marini, 2007; Ming & Franklin, 1985; Xiong & Lord, 2008) have reported the effects of temperature and CO_2 concentration on the formation, stability and transformation of various Mg-carbonates, albeit not in the cement context. The formation of lansfordite and artinite was observed in ambient temperatures and CO_2 concentrations (Königsberger 1999; Ming & Franklin, 1985), whereas other studies (Marini, 2007) reported the formation of hydromagnesite

under similar conditions as the formation of artinite was suggested to require less CO₂ than the amount present at ambient levels (e.g. $8\text{--}40 \times 10^{-4}$ vs. 0.04%). Apart from ambient conditions, the formation of hydromagnesite was also observed under elevated temperatures ($> 40\text{ }^{\circ}\text{C}$) (Königsberger 1999; Marini, 2007; Xiong & Lord, 2008), preceding the formation of magnesite at around $120\text{ }^{\circ}\text{C}$ (Botha & Strydom, 2001; Hänchen 2008).

Alternatively, increasing the CO₂ concentration at ambient temperatures is known to lead to the formation of nesquehonite (Davies & Bubela, 1973; Königsberger 1999; Xiong & Lord, 2008). Different CO₂ levels of around 0.034–0.035% have been suggested regarding the boundary above which the formation of nesquehonite commences (Königsberger, 1999; Xiong & Lord, 2008). Lansfordite was also reported to form under similar conditions but at lower temperatures and CO₂ concentrations than nesquehonite (Ming & Franklin, 1985). The stability of nesquehonite, which is governed by not only temperature but also the water activity and CO₂ concentration, was reported by several studies (Davies & Bubela, 1973; Dell & Weller, 1959; Lanas & Alvarez, 2004; Langmuir, 1965; Ming & Franklin, 1985). Nesquehonite is stable under natural conditions and is widely synthesized for different processes including CO₂ sequestration (Ballirano, De Vito, Ferrini & Mignardi, 2010a; Ferrini, De Vito & Mignardi, 2009a), where it was shown that its structure can remain substantially unaffected at up to $100\text{ }^{\circ}\text{C}$ (Ballirano 2010a). Alternatively, some studies (Hopkinson 2012) have claimed that nesquehonite can decompose into more stable carbonates at temperatures above $52\text{ }^{\circ}\text{C}$.

2.7 Durability of PC concrete

2.7.1 Chloride penetration

Chloride penetration is associated with the corrosion of reinforcement in concrete, which can cause structural failure due to rust formation. Under normal conditions, steel reinforcement is protected by the high pH of the pore solution in concrete, which forms a

stable passive film surrounding the steel. In the hydrated PC systems, the formation of hydrate phases such as Ca(OH)_2 maintains a pH of above 12. In carbonated systems, the passive film tends to be unstable at a pH of < 11.5 , resulting in the leaching out of calcium and ingress of chloride ions. In such circumstances, rusting can take place, which leads to expansion and cracking in concrete (Chia & Zhang, 2002; Shi, Xie, Fortune & Gong, 2012; Song, Lee & Ann, 2008; Stanish, Hooton & Thomas, 2000).

2.7.2 Sulfate attack

Sulfate attack takes place when concrete samples are exposed to sulfate solutions of sodium, magnesium or calcium (Bakharev, Sanjayan & Cheng, 2002; Santhanam, Cohen & Olek, 2003). Sulfates exist in soil, natural or polluted ground water and industrial wastes. For example, exposure to sodium sulfate (Na_2SO_4) solution may lead to both sulfate attack and alkali silica reaction in PC-based concrete mixes. For sulfate attack to occur in concrete mixes, a number of conditions must be satisfied, such as the presence of sulfates and mobile groundwater, as well as the formation of Ca(OH)_2 and calcium aluminate hydrate (C-A-H) in the cement matrix. Sulfate attack can cause swelling in concrete, as well as strength and durability loss via the expansive formation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) in the presence of H_2O , Ca^{2+} (i.e. from the dissolution of hydrate phases) and SO_4^{2-} (i.e. from the external solution). The formation of these phases results in concrete deterioration initially via the loss of stiffness and strength, followed by expansion and cracking (Marchand, Odler & Skalny, 2003). The presence of thaumasite ($\text{Ca}_3\text{Si(OH)}_6(\text{CO}_3)(\text{SO}_4) \cdot 12\text{H}_2\text{O}$) at temperatures below 15°C has also been associated with sulfate attack, which leads to the formation of a soft, incohesive white mass (Crammond, 2003).

2.7.3 Freeze-thaw cycling

Freeze-thaw cycling, which can be found in cold areas, causes damage to concrete structures due to their porous nature. Deterioration is caused by the freezing of water and its subsequent expansion in concrete. Water exists in the pores of concrete and expands to about 9% of its initial volume when it freezes. When the pores are saturated, the lack of room for expansion can develop pressure in the pores, which leads to crack formation once it exceeds the tensile strength of the concrete. During the thaw process, more water is absorbed into the pores, resulting in the formation of new micro-cracks. Under the accumulative effect of successive freeze-thaw cycles, the bonds between the cement paste and aggregates gradually break and eventually cause cracking, scaling, and crumbling of the concrete (Polat, Demirboğa, Karakoç & Türkmen, 2010; Qin 2016). This effect can be more pronounced in the presence of deicing salt such as NaCl, CaCl₂ and MgCl₂ as these reduce the freezing point and result in the progressive removal of small pieces of paste within the surface of concrete, also known as salt scaling. Furthermore, the use of deicing salt can also increase the risk of chloride attack in concrete (Liu & Hansen, 2016; Shi, Fay, Peterson & Yang, 2010).

2.7.4 Seawater exposure

Concrete structures exposed to marine environments (i.e. usually for the production and transmission of electricity, oil or gas) usually suffer from physical and chemical deterioration in seawater. The physical causes of concrete deterioration under seawater include surface wear by abrasion and cavitation, expansion and micro-cracking due to pressure from salt crystallization (Mehta, 2002). These physical deteriorations facilitate ion ingress and subsequent harmful chemical interactions between seawater and the hydrate phases in concrete mixes. The high concentrations of chloride and sulfate in sea water can lead to chloride and sulfate attacks, which cause deterioration in concrete. Chemical decomposition and leaching of the constituents of the hydrate phases in the cement paste give rise to detrimental physical effects, such as increase in porosity and therefore loss of

strength (Binici, Aksogan, Görür, Kaplan & Bodur, 2008; Ganjian & Pouya, 2005; Pack, Jung, Song, Kim & Ann, 2010).

2.8 Potential applications for MgO cements

Construction blocks are a promising application for reactive MgO cements (Harrison, 2001). The main advantages of blocks are: (i) suitability for sequestering CO₂ due to their initially porous structure; (ii) lack of need for in-situ treatment as carbonation can take place during fabrication; and (iii) high potential for commercialization, supported by a large volume of research (Liska, 2009; Liska & Al-Tabbaa, 2008; Liska & Al-Tabbaa, 2009; Liska & Al-Tabbaa, 2012; Liska, Al-Tabbaa 2012a; Liska, Al-Tabbaa & Fifield, 2012; Liska, Vandeperre & Al-Tabbaa, 2008; Unluer, 2012; Unluer & Al-Tabbaa, 2011; Vandeperre 2007).

Several studies have investigated hydration (Jin, Abdollahzadeh & Al-Tabbaa, 2013; Jin & Al-Tabbaa, 2013b; Rocha, Mansur & Ciminelli, 2004; Thomas, Musso, Prestini & Troczynski, 2014; Vandeperre, Liska & Al-Tabbaa, 2008) and microstructure (Mo & Panesar, 2012; Vandeperre 2008b) of MgO and MgO-PC systems, some of which contained PFA and GGBS. Much attention has been given to the high CO₂ sequestration potential of MgO (Chang & Chen, 2006; Bertos, Simons, Hills & Carey, 2004; Ferrini, De Vito & Mignardi, 2009; Hovelmann, Putnis, Ruiz-Agudo & Austrheim, 2012; Jia, Anthony, Lin, Ruan & Gora, 2004; Mo & Panesar, 2012; Mo & Panesar, 2013; Orlando, Lelli & Marini, 2012; Thiery, Villain, Dangla & Platret, 2007; Unluer & Al-Tabbaa, 2013, 2014; Vandeperre & Al-Tabbaa, 2007) and the associated strength gain and microstructural development due to carbonation of mixes with varying compositions of MgO, PC and/or PFA and/or GGBS. The rate of carbonation depends on several factors such as the reactivity, overall porosity and the connectivity of the pores, cross section of the member and the curing conditions. Recent studies on porous blocks include durability tests using hydrochloric acid and magnesium sulfate solutions (Liska, 2009; Liska & Al-Tabbaa, 2012) and the effect of mix design in MgO-PC and MgO-PC-GGBS systems (Panesar & Mo,

2013), curing conditions (Unluer, 2012; Unluer & Al-Tabbaa, 2014), aggregate profile (Unluer, 2014; Unluer & Al-Tabbaa, 2012) and use of additives (HMCs, brucite, and other magnesium silicates) (Unluer & Al-Tabbaa, 2013; Unluer & Al-Tabbaa, 2015) on the rate and extent of carbonation.

The strength gain of MgO and PC pastes and aggregate-cement masonry units has been investigated (Vandeperre 2007). While 80% of the paste mixes were composed of PFA, the remaining 20% was either MgO, PC or a mix of both in equal weights (10% each). The strengths of mixes cured at ambient CO₂ increased with the amount of PC, reaching 24 MPa, 7 MPa, and 1 MPa for those containing only PC, both PC and MgO in equal amounts, and only MgO, respectively. With the introduction of accelerated carbonation at 20% CO₂ concentration under a RH of 80-90%, the 28-day strength of pastes containing only MgO increased from 1 to 6 MPa, which was still less than the 28-day strength of PC systems cured under ambient conditions. When the pastes were replaced by aggregate-cement masonry units incorporating 10% cement, mixes containing only MgO outperformed all other mixes with 28-day strengths of ~18 MPa under accelerated carbonation due to the increased penetration of CO₂ through the porosity provided by the imperfect packing of aggregates. Further reductions in the cement content and CO₂ concentration could be used to achieve the strength requirement of 7 MPa for masonry units according to the standard BS EN 771-3:2011/A1.

Some of the applications where blocks are widely used include construction of road side paver, garage and parking floorings, driveways, walls, and floor coverings of commercial buildings. The length, width and thickness of rectangular concrete paving blocks vary from 200 to 240mm, 100 to 160mm, and 60 to 140mm, respectively. Some studies investigated the mechanical performance of PC blocks (i.e. compressive strength, tensile strength, water absorption, abrasion resistance, etc.) in terms of mix design (i.e. cement and water content, adding SCMs) and curing conditions (i.e. humidity and duration) (Lam, Poon & Chan, 2007; Langley 1992; Poon & Lam, 2008; Sukontasukkul & Chaikaew, 2006). Very limited amount of work has been reported on the production of MgO blocks on a large scale so far (Liska, Al-Tabbaa, Carter & Fifield, 2012b). These studies briefly highlighted the influence

of certain factors (i.e. water content and particle size distribution) on the final mechanical performance of large scale MgO blocks (440 x 100 x 215 mm).

3. EXPERIMENTAL METHODS

This chapter presents the properties of the raw materials including cement binder, aggregates and supplementary cementitious materials (i.e. pulverized fly ash (PFA) and ground granulated blast-furnace slag (GGBS)) used in this research. Preparation and curing of paste and concrete samples are reported. This is followed by the details of the test methods in the analysis of the results. Methods for analyzing the properties of raw materials, the mechanical performance and microstructure of cement samples are presented. Testing specimen preparation, key aspects of interpretative procedure and special precaution to ensure accurate results are shown.

3.1 Raw materials

3.1.1 Cement binder

Magnesium oxide (MgO) and Portland cement (PC) were the two types of cement binders used in this study (Figure 3.1). Two types of MgO were used in different studies: MgO_{92/200} was supplied by RBH Ltd, UK and MgO 90% was obtained from International Scientific, Singapore. The ordinary PC was obtained from Lafarge Singapore. Table 3.1 presents the chemical composition of both of these binders. The main impurities present in PC are SO₃, Fe₂O₃ and Al₂O₃. The XRD pattern of two types of MgO are presented in Figure 3.2. While the MgO indicates a 91.5% purity level, its major impurities include SiO₂ and CaO. From the XRD pattern, the presence of magnesite was from the incomplete calcination of the parent material (magnesite) during the production of MgO, and the presence of brucite was due to the partial hydration of MgO during transport and storage (i.e. before sample preparation). MgO 90% has higher impurities compared to the MgO_{92/200}. The particle size distribution (PSD) of MgO_{92/200} and PC is presented in Figure 3.3. Although PC is

composed of slightly coarser particles, both powders follow a similar size distribution, which indicates their compatibility within the mixes designed under this study.

Table 3.1 Chemical compositions of MgO and PC from suppliers' datasheets

	MgO	SiO ₂	CaO	SO ₃	Fe ₂ O ₃	Al ₂ O ₃
MgO _{92/200}	91.5	2.0	1.6	-	-	-
MgO 90%	> 90	< 5	5.0	-	-	0.7
PC	0.92	20.89	66.2	2.38	3.87	6.08

Figure 3.1 PC and MgO used in the study

(a)

(b)

Figure 3.2 XRD pattern of (a) $\text{MgO}_{92/200}$, and (b) MgO 90%

Figure 3.3 Particle size distribution of MgO and PC

3.1.2 Aggregates

Sand and gravel (9mm chipping) were supplied by Buildmate Pte Ltd, Singapore, and used as the source of natural aggregates (Figure 3.4). The PSD of the fine and coarse aggregates, along with their mixture is shown in Figure 3.5. The particle sizes of these aggregates range between 0.1mm and 10mm. Sand clearly has a smaller PSD than gravel. The grading curve of their mixture shows an evenly distributed profile.

Figure 3.4 Sand and gravel used in this study

Figure 3.5 Particle size distributions of the coarse and fine aggregates

3.1.3 PFA and GGBS

PFA (class F) and GGBS were used as supplementary cementitious materials to replace part of the cement binder in some of studies in this report. PFA (class F) and GGBS, shown in Figure 3.6, were provided by Bisley Asia (Singapore) and EnGro (Singapore), respectively. Table 3.2 presents the chemical composition of PFA and GGBS. The average particle sizes of PFA and GGBS were 10-20 μm and $<5 \mu\text{m}$ from the supplier, respectively.

Figure 3.6 (a) PFA and (b) GGBS used in this study

Table 3.2 Chemical compositions of PFA and GGBS from suppliers' datasheets

	Chemical composition (%)						
	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	-	-

3.2 Sample preparation and curing

3.2.1 Sample preparation

3.2.1.1 Concrete cylinder sample preparation

The concrete cylinder samples used in this study were prepared according to the following procedure:

1. A dry mix of typically 3-3.5 kg material (MgO/PC + aggregates) are prepared and mixed using a laboratory-scale concrete mixer. Once the dry contents are thoroughly mixed, water is gradually added to the mixing bowl.
2. As soon as the concrete mix is prepared, 300 grams of the prepared mix was placed into metal cylindrical moulds 50mm in diameter.
3. The mix placed in the cylindrical moulds was pressed manually to a pressure of 3 metric tons.
4. Once pressing was completed, the mould was dismantled and the sample inside was carefully removed and placed into respective curing environments.

The resulting samples have a diameter of 50mm and a height of 65-75 mm. The mass of all samples was measured immediately after demoulding and recorded before placing them in their respective curing environments.

3.2.1.2 Concrete cubic sample preparation

The concrete cylinder samples used in this study were prepared according to the following procedure:

1. A dry mix of typically 3-3.5 kg material (MgO/PC + aggregates) are prepared and mixed using a laboratory-scale concrete mixer. Once the dry contents are thoroughly mixed, water is gradually added to the mixing bowl.
2. After the mixing process, all samples were cast into 50×50×50 mm cubic specimens
3. Samples were consolidated using a vibrating table and trowel finished.

The resulting samples have a dimension of 50×50×50 mm. The prepared samples were demolded after 24 hours and subjected to curing.

3.2.2 Curing conditions

Two different curing conditions were employed in this study: (i) natural and (ii) accelerated curing. The environments in which both curing conditions took place are shown in Figure 3.7. The CO₂ concentration, temperature, and RH values used in both curing environments are listed in Table 3.3. For natural curing, samples were placed in plastic containers in which water was added right below the board on which the samples were placed to keep the RH constant at ~90% at all times. MgO and PC samples were cured for up to 6 months due to the lower carbonation rate in ambient conditions. For accelerated carbonation, samples were placed in a CO₂ incubator in which the CO₂ concentration was adjusted to 10% for up to 56 days.

Figure 3.7 The two curing conditions used in this study (a) natural, and (b) accelerated.

Table 3.3 Parameters of two curing conditions

Carbonation condition	Facility	Temperature	Humidity	CO ₂ concentration
Natural	Plastic container	30°C	92%	Ambient
Accelerated	CO ₂ incubator	30°C	97%	10%

3.2.3 Pre-conditioning

Before normal carbonation curing, MgO cement samples were placed in an environment chamber (Figure 3.8), and subjected to elevated temperatures between 40 and 60 °C, whereas the humidity was fixed at 90%. The pre-conditioning process lasted for 1 to 2 days.

Figure 3.8 Environmental chamber used for pre-conditioning

3.3. Testing methodology

This section includes a detailed description of all the characterization and mechanical testing methodology used under this study.

3.3.1 Standard consistency (SC)

The SC of MgO and PC pastes were measured with a Vicat apparatus (Figure 3.9). The SC of each binder was used to determine the amount of water required to produce workable mixes. It is defined as the percentage of water by weight of dry cement when the Vicat plunger penetrates at a certain depth of the paste corresponding to a reading on the gauge ranging between 5-7mm. To enable this, 400 gram of cement powder was mixed with water and placed in the Vicat apparatus with an even and smooth surface. The plunger was then placed just above the paste and the plunger was allowed to sink into the paste. The entire test was completed within 5 minutes before the paste hardened. As a result of this test, the water content was determined as a weight percentage of the dry cement content in the mix. The test was performed on individual components and pastes.

Figure 3.9 Vicat apparatus used for SC measurements

3.3.2 Particle size distribution (PSD)

PSD of the materials was calculated in order to determine the exact proportion of the particles over a range of sizes. The PSD of the aggregates also revealed the packing arrangement of the different ratios of fine and coarse aggregates along with the voids between the particles, which influences the diffusion rate of CO₂ and the formation of different phases. This information was later be used to determine whether the aggregate used complies with the specific design in mind, to observe the relationships (e.g. particle packing) between various aggregate blends, and to make predictions regarding trends during production by plotting gradation curves at the end of the sieve analysis.

PSD of the aggregates was obtained by sieve analysis (Figure 3.10). To enable this, the aggregates were passed through a series of sieves with different sizes ranging between 0.3 – 10 mm. After vibration, the total amount of aggregate remaining on each sieve was recorded and used to plot the final grading curve. In addition to the aggregates, the PSD of cement powders (MgO and PC) was conducted on a Masterier 2000 optical system (Figure 3.11). The sieves were placed by descending order of sieve size from the top to the bottom on an electric shaker, around 1 kg aggregate was placed on the sieves and shaken for 3 minutes.

Figure 3.10 Equipment used for the sieve analysis of natural aggregates

Figure 3.11 Masterier 2000 optical system used to measure the PSD of cement powders

3.3.3 Density

Samples were weighted before and after curing, and their heights obtained to calculate the changes in mass and density before and after carbonation in accordance with the equation below:

$$D = \frac{w_{after} - w_{before}}{\pi * r^2 * h} \quad (3.1)$$

where w_{after} and w_{before} is weight of samples before and after curing.

3.3.4 Porosity

The porosities of the samples before and after curing were calculated by the following equation according to ASTM C642-06:

$$p = \frac{m_{sat} - m_{dry}}{v} * 100 \quad (3.2)$$

where m_{sat} is the weight of samples saturated in water (i.e. until constant mass was obtained), m_{dry} is the weight of dry samples at 70 °C for 3 days (i.e. to ensure the evaporation of all free water), and v is the volume of samples.

3.3.5 Carbonation depth measurement by pH indicator (phenolphthalein)

Carbonation degrees at different depths were studied by phenolphthalein indicator to determine the depth of carbonation under different conditions. Phenolphthalein indicator will turn pink in alkaline conditions (i.e. at a pH of > 0), which indicates the existence of hydration products such as $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$. As carbonation proceeds, the area on which phenolphthalein indicator is dropped becomes colorless when the pH is 8.2, showing that carbonation is complete. Three sections along the length of each sample were sprayed with phenolphthalein indicator to establish a carbonation depth profile at different curing durations. The obtained results were compared with the carbonation degree results measured by XRD and TGA.

3.3.6 pH measurement

The pH of the samples was conducted in accordance to ASTM C 25. To get a final reading, 5 gram of sample powder was placed into 100 gram of distilled water and stirred for 30 minutes and allowed to stand for 30 minutes. All measurements were conducted in triplicates and the average values were recorded. Measurement of the solution pH was performed by using a Mettler Toledo pH meter (Figure 3.12).

Figure 3.12 pH meter setup

3.3.7 Unconfined compressive strength (UCS)

The UCS of the samples was measured at different curing durations by uni-axial loading in triplicates in accordance with the specifications of ASTM C39/C39M-16 via an Axiomtek compressing machine (Figure 3.13). The load was applied at a rate of 100 kN/min.

Figure 3.13 Unconfined compressive strength test

3.3.8 Chloride penetration test

The silver nitrate (AgNO_3) spray test was used to measure the chloride penetration in samples subjected to chloride attack, freeze-thaw cycling and seawater exposure. To initiate the measurement, 0.1 mol/L AgNO_3 aqueous silver nitrate solution was sprayed onto the cross section of a freshly split concrete sample. In most cases, the chloride-affected zone appeared light grey or white, whereas the chloride-free zone was dark grey or black. As the use of PFA/GGBS in the mix design may influence the color interpretation, only MgO samples were studied via this approach. The average chloride penetration depth (x_d) was obtained by observation, for which a ruler with an accuracy of ± 0.5 mm was used to measure the actual depth ranging from the location of the penetration front to the surface. Five measurements were conducted and the average values were recorded for each sample. The concentration of chloride at different sample depths was calculated by Fick's second law, as shown in Equation 3.3, where C_x is the concentration at depth x (mm) after time t (day), C_s is the surface concentration, erf is the error function and D_{app} is the apparent diffusion coefficient, which can be calculated according to Equation 3.4, where C_d is the chloride concentration at the color change boundary which is fixed at 0.07 mol/L from previous study (He, Shi, Yuan, Chen & Zheng, 2012).

$$C_x = C_s \left(1 - \text{erf} \frac{x}{2\sqrt{D_{\text{app}}t}} \right) \quad (3.3)$$

$$D_{\text{app}} = \left(\frac{x_d}{2\text{erf}^{-1}\left(1 - \frac{C_d}{C_s}\right)\sqrt{t}} \right)^2 \quad (3.4)$$

3.3.9 Scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM)

Samples extracted from the concrete samples crushed during strength testing were stored in acetone to stop hydration, followed by vacuum drying in preparation for XRD, TGA and SEM-EDX analyses.

Scanning electron microscopy (SEM) was used for the acquisition of highly magnified images (up to 10,000 times) of the surface of a solid specimen. SEM was performed via a Zeiss EVO50 to identify hydration and carbonation products in the samples subjected to different curing conditions. FESEM was also utilized to provide quantitative information of chemical elements that formed due to hydration and carbonation reactions (Figure 3.14). To prepare the samples for each analysis, the blocks were first crashed into small pieces and those from the inner part of the blocks selected. Samples were held to metal stubs using conductive double coated carbon tape. Then samples were spatter coated with ~15 nm platinum after mounting the specimen to increase conductivity of samples and avoid sample charging under electron beam. The accelerated voltage used for the work was between 5 and 15 kV depending on the extent of undesirable charging. The low vacuum mode was also used to eliminate charging. Samples were scanned and images were captured at different magnifications from 1000 to 5000 times.

Figure 3.14 Equipment used for (a) SEM and (b) FESEM analysis

3.3.10 Thermogravimetric/differential thermal analysis (TG/DTA)

Thermogravimetry/differential thermal analysis (TG/DTA) is a useful tool in cement chemistry for studying hydration reactions (Fordham and Smalley, 1985; Ramachandran, 1988), identifying phases formed (Ray 1995), and studying the effects of pozzolanic

additives (Kasselouri 1983; Slanička 1985). TGA was conducted on a Perkin Elmer Diamond Thermogravimetric-differential thermal analysis (Figure 3.15). The analysis was run from 40 to 900 °C with a heating rate of 10°C/ minute in nitrogen flow. The small pieces for SEM were ground into powder passing through a 125 µm sieve. To ensure the accuracy of the results, weight and temperature calibration are carried out every two months. Silver foil sample is used for weight calibrations to make sure the weight measured by thermo-balance is the same with known sample weight.

TGA provides a valuable tool for quantifying the degree of hydration (H₂O vapor emitted during the decomposition of brucite) and carbonation (CO₂ gas emitted during the decarbonation of magnesite into MgO) by measuring the concentration distributions of Mg(OH)₂ and MgCO₃. Before the analysis, MgO pastes were stored in acetone for at least 3 days to quench hydration and dried in a vacuum for at least 7 days to remove any remaining moisture. The samples were heated from 50 to 600 °C with a heating rate of 10 °C/min under nitrogen flow. The weight loss L (%) corresponding to the dehydration of brucite was used to calculate the hydration degree (HD) of MgO shown in Equation 3.5, where C is the actual MgO content as a percentage of the total cement component. 40 and 18 are the molecular weights of MgO and H₂O, respectively.

$$HD = [L \times 40/18]/[1 - 0.01L] \times C \text{ (\%)} \quad (3.5)$$

Figure 3.15 Equipment used for TG analysis

3.3.11 X-ray Diffraction (XRD)

X-Ray diffraction (XRD) was employed to obtain the chemical composition of the crystalline phases in the sample. The samples subjected to compressive testing were ground into powder passing through a 125 μm sieve in preparation for XRD analysis, which was conducted on a Bruker D8 Advance powder diffractometer with a $\text{Cu K}\alpha$ source to analyze the presence of crystalline phases in the prepared mix formulations. A scanning range (2θ) of 5 and 80 $^\circ 2\theta$, with a scanning rate of 1s/step and a step size of 0.04/step was used (Figure 3.16a). Phase quantification was performed via the Rietveld refinement software TOPAS 5.0 with a fundamental parameters approach (Figure 3.16b). The basic principle of the method is a description of all data points of a powder pattern using analytical and/or numerical functions. The parameters of these functions, consisting of crystal structure, sample, instrument and background parameters, are refined simultaneously using least squares methods. The results are less reliable when the percentage content of a phase is lower than 2%. A similar approach was used in several previous studies involving the use of cement-based systems (Ruan & Unluer 2017a; Cordeiro, Filho, Tavares & Fairbairn 2009; Scrivener, Füllmann, Gallucci, Walenta & Bermejo 2004; Saoût, Kocaba, Scrivener 2011).

(a)

(b)

Figure 3.16 (a) Equipment used for XRD analysis (b) quantification by TOPAS

3.3.12 HCl acid test

HCl acid test was applied to evaluate the CO₂ uptake in samples based on the neutralization of carbonation products (Figure 3.17). This process involves the reaction between CO₂-containing solution and HCl acid (Equation 3.6, 3.7) To achieve this, 40 ml HCl acid solution were poured into a beaker with 30 grams of sample, and the weight before and

after the reaction recorded. The relatively high molarity used caused the reaction to take place at a rapid pace, thereby providing results in a short time without incorporating the volatility of the acid solution. To ensure a fast reaction, samples were ground into fine powder and placed into a high concentration HCl acid solution (3M/L).

Figure 3.17 Quantifying the CO₂ content by HCl acid test

3.3.13 Isothermal calorimetry

The heat flow and cumulative heat evolved due to the hydration of each mixture were studied at 30 °C by an I-Cal 2000 High Precision Calorimeter in accordance with ASTM C1702-15a (Figure 3.18). Cement paste samples were prepared to study the hydration rate and hydration degree of the MgO cement paste cured at different temperatures for up to 7 days. The prepared mix was instantaneously placed into the isothermal calorimeter channel to ensure the accuracy of results.

Figure 3.18 Equipment used for isothermal calorimetry

3.3.14 ICP-OES/IC

The content of ions such as Na^+ and Mg^{2+} were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) conducted on a Elements Perkin Elmer Optima 8000, whereas the contents of Cl^- and SO_4^{2-} were measured by ion chromatography (IC). The sample solution was filtered and diluted 500 times. ICP-OES test is carried out by original calibration solutions from PerkinElmer. The detection limit of Na and Mg was 0.001ppm. A Quality Check is conducted after calibration to ensure accuracy of calibration curve. IC test is carried out by running calibration using the Combined Seven Anion Standard II. The calibration standard for Cl^- are with this concentration: 0.75ppm, 1.5ppm, 3ppm & 6ppm. The calibration standard for SO_4^{2-} are with this concentration: 3.75ppm, 7.5ppm, 15ppm & 30ppm.

Figure 3.19 Perkin Elmer Ion chromatography system

4. INFLUENCE OF THE MIX DESIGN AND CURING CONDITIONS ON THE PERFORMANCE AND MICROSTRUCTURE OF MGO CEMENT CONCRETE

This chapter is divided into two parts, studying the effects of mix design and pre-conditioning on performance and microstructure of MgO cement concrete. The initial part of the study investigates the strength and microstructural developments of a range of MgO cement concrete formulations subjected to 10% CO₂ curing for up to 28 days. Each mix composition includes 5–10% cement and 85–90% natural aggregates at two different w/c ratios. The density, porosity, compressive strength, carbonation depth, CO₂ uptake and morphology of each formulation are reported at different depths along the sample cross-sections. This is followed by the second part, which uses a pre-conditioning method to enhance the hydration and carbonation MgO cement concrete. Hydration degree under different pre-conditioning is studied by calorimetry method and TGA on paste samples. Microstructure change and quantitative analysis of the composition of the samples under different pre-conditioning after 56 days of curing are studied by XRD, TGA and SEM.

4.1 Study 1: Influence of mix design (i.e. cement and water content)

4.1.1 Introduction

Although there are previous studies investigating the influence of cement/water content on carbonation of MgO cement (Liska & Al-Tabbaa, 2009; Unluer & Al-Tabbaa, 2012; Vandeperre & Al-Tabbaa, 2007; Unluer & Al-Tabbaa, 2011),

supplementary cementitious materials (i.e. pfa) was used in those studies, which might change the carbonation mechanism of pure MgO cement system in this study. Besides, most of the previous studies on carbonated MgO mixes report the overall degree of carbonation within the prepared samples, without providing detailed info on the extent of carbonation within the sample cross-section and the implication of this on the mechanical performance. This research investigates the carbonation potential, strength gain and microstructural development of MgO cement concrete blocks and provides a comparison with PC concrete blocks. The density, porosity, compressive strength, carbonation depth, CO₂ uptake and morphology of each formulation were reported at different depths along the sample cross-sections. The relationship between performance and CO₂ uptake; and the influence of key parameters on the carbonation, microstructure and mechanical performance of MgO-based samples was established.

4.1.2 Mix design

Reactive MgO and PC were the two types of cement binders used in this study. Four block mix designs containing 5-10% cement and 90-95% aggregate by weight were prepared under this study. The aggregates were natural sand and gravel, whose ratio was kept constant at 10:7 for all mixes. The detailed mix compositions are presented in Table 4.1. The cement binder was composed of: (i) MgO alone (mixes labelled as M10_H, M10_L, M5_H, M5_L), (ii) PC alone (mixes labelled as P10_H, P10_L, P5) and (iii) a combination of MgO and PC (mixes labelled as MP_H, MP_L). For all mix labels, the first letter (M, P or MP), the adjacent number (10 or 5), and the following letter (H or L) represent the cement type (MgO, PC, or MgO and PC), cement content (10% or 5% by weight of the dry mix) and the water content (high or low), respectively. Two different w/c

ratios equivalent to the standard consistency (SC)+11% and SC+27% were used for each composition, resulting in two standard levels of workability for each mix design. This was applied to all mixes except for mix P5, for which the w/c ratio had to be increased from the calculated 0.38 to 0.5 due to the small binder content.

Table 4.1 Mix compositions investigated under this study

Mix label	Cement content		Aggregate content		w/c ratio
	MgO (%)	PC (%)	Gravel (%)	Sand (%)	
M10 _H	10	0	53	37	0.80
M10 _L					0.70
P10 _H	0	10	53	37	0.42
P10 _L					0.38
M5 _H	5	0	56	39	0.80
M5 _L					0.70
P5	0	5	56	39	0.50
MP _H	5	5	53	37	0.61
MP _L					0.54

4.1.3 Results and discussion

4.1.3.1 Compressive strength

Blocks consisting of 5-10% cement (10% MgO, 10% PC, 5% MgO + 5% PC) and 2 levels of water content corresponding to SC+11% and SC+27% were cured under 10% CO₂ for 1, 3, 7, 14, and 28 days before being tested for their compressive strengths. Samples were tested in triplicates and the average value and standard consistency were calculated for each data point. The strength test

results of all blocks to 28 days are shown in Figure 4.1. The maximum strength reached by MgO and PC blocks over 28 days of curing are recorded as 25 and 13 MPa, respectively. As shown in Figure 4.1, 10% MgO blocks have the highest strength results, followed by 5% MgO + 5% PC blocks, 10% PC, 5% MgO and 5% PC samples. Strength results of 10% MgO blocks with a w/c ratio of 0.8 is 83% higher than those of 10% PC blocks after 7 days curing, indicating the obvious advantage of MgO blocks over PC blocks under accelerated curing. For all samples, strength gain mainly occurs within the first 7 days, which then slows down due to the blocking of initially available pores by the newly formed carbonate products. As carbonation proceeds, the reduction in porosity hinders the diffusion of CO₂ and thus decreases the carbonation rate and strength gain. Some strength loss observed in the case of MgO blocks after 14 days can be attributed to the drying of the blocks due to the limited humidity in the incubator, which hinders the carbonation process and may result in small cracks depending on the extent of drying.

The strength development of MgO blocks is presented in Figure 4.2. The results show that samples containing 10% MgO have higher strengths than those with 5% MgO. This is because the increased cement content provides better binding properties and fills the voids between aggregates to form a better compaction with a denser structure. Among the 10% MgO samples, blocks with higher water contents (w/c of 0.8) have lower strengths than corresponding blocks with a w/c of 0.7 during the first 3 days. As carbonation proceeds, samples with a w/c of 0.8 exceed the strength of corresponding blocks with lower water contents (w/c of 0.7). A possible explanation for this trend is that at early stages, the excess water present in the samples with a w/c of 0.8 blocks the available pores and hinders the penetration of CO₂ into the samples, which happens faster in partially saturated samples (w/c of 0.7). After 3 days, once the extra water is consumed by the carbonation reaction, the excess water present in the samples

with higher initial water contents (0.8) can promote further carbonation, thereby experiencing an increase in strength gain.

Figure 4.3 shows the strength results of PC blocks cured under the same conditions. Samples containing 10% PC have higher strengths than those containing 5% due to the higher availability of the binder content in the former. Unlike MgO mixes, which develop strength via the carbonation process, the strength gain of PC mixes mainly depends on the hydration process during which calcium silicate hydrate (C-S-H) and portlandite (Ca(OH)_2) forms. Subjecting PC mixes to carbonation the hydration products convert into CaCO_3 , which has porous structure, resulting in strength loss.

The strength requirement of masonry blocks for commercial use is 7 MPa according to the standard BS EN 771-3:2011/A1. As the prepared 10% MgO samples can achieve strengths higher than 10 MPa in only 1 day of curing is a clear indication of the feasibility of using MgO cements on a larger scale in the production of similar construction blocks.

Figure 4.1 Compressive strength of all blocks up to 28 days of curing under 10% CO_2

Figure 4.2 Compressive strength of MgO blocks up to 28 days of curing under 10% CO₂

Figure 4.3 Compressive strength of PC blocks up to 28 days of curing under 10% CO₂

4.1.3.2 Density

Figure 4.4 shows the change in densities of all blocks from 1 to 28 days of curing. The initial densities of M10, P10, MP, and M5 samples ranged between 0.8, - 0.4, 0.1, and 0.5 unit. The average increase in the densities M10, P10, MP, and M5 samples over 28 days of curing were 4.1%, 0.9%, 1.4% and 2%. The trend of density change is similar to that of strength development, which indicates the direct relationship between the density and final strength of blocks. An increase of up to 4% is observed in the densities of samples during the first 7 days. The highest increase in density is achieved by MgO blocks, followed by MgO+PC blocks. A negligible change in the densities of PC blocks was seen after 7 days of curing. Figure 4.5 shows the density changes of MgO blocks, the increase in the densities of MgO blocks is achieved by the expansive progress of carbonation. The formation of HMCs as a result of this reaction causes a decrease in the overall porosity of samples, hence increasing their density. More HMCs formed in 10% MgO and thus higher density can be observed 10% MgO sample than 5% samples. This reaction takes place much faster during the first 7 days of curing, after which it slows down as the initially available pores are filled with carbonation products, hindering the further diffusion of CO₂ into the pore system. The reduction in densities observed in some blocks (e.g. M5 samples) may be linked with the drying out of the samples due to the lack of humidity required for the continuation of hydration and carbonation reactions in the curing environment.

Figure 4.4 Changes in the density of all blocks over 28 days of accelerated curing

Figure 4.5 Changes in the density of MgO blocks over 28 days of accelerated curing

4.1.3.3 Porosity

The porosities of blocks with different compositions measured according to Equation 3.2 after 1 and 14 days of curing are shown in Figure 4.6. 16.2%, 18.1%, 10.2%, and 2.5% decreases in the porosities of M10, P10, MP, and M5 samples were obtained from 1 to 14 days of carbonation, respectively, and porosity trended inversely with density. An increase in the MgO content causes a further reduction in porosity. Similar to the increase observed in the densities of these blocks over time, the reduction in porosity is attributed to the formation of hydration and carbonation products within the pore system, resulting in strength gain.

Figure 4.6 Porosity change of M10 and P10 samples

4.1.3.4 XRD

The XRD patterns of M10_H samples after 1 day of curing are presented in Figure 4.7. Nesquehonite (PDF # 020-0669) is observed at its two strongest peaks at 13.7° and 23.1° 2θ, confirming its presence. Dypingite (PDF # 029-0857) has

its four highest intensity peaks at 15° , 30.4° , 13.7° and 21° 2θ followed by peaks with similar lower intensity at 12° , 20° , 27.9° , 41.3° , 45.5° , and 44.8° 2θ . All the 4 strong peaks and many of the weaker ones can be seen in the XRD patterns presented, confirming the presence of dypingite. Hydromagnesite (PDF #025-0513) has its highest intensity peaks at $\sim 15.3^\circ$, 30.8° and 13.7° 2θ , which are similar to those of dypingite and hence are expected to overlap on the XRD spectra. Hydromagnesite (PDF # 003-0093) also has sharp peaks in the high-angle region at 42° and 45.5° 2θ , where small peaks can be seen in the presented diffractograms. These peaks confirm the presence of hydromagnesite in the samples.

Based on the peak intensities, the presence of various HMCs such as dypingite, hydromagnesite and nesquehonite was observed. The relatively low intensities of these HMCs in each sample was due to the heavy presence of aggregates, which made up 90% of the overall mix by weight, as indicated by the quartz peaks. Although the inclusion of aggregates was crucial for the preparation of representative samples, this presented a challenge in the identification of HMC peaks that overlapped with quartz. The intensities of HMC peaks reduced as the sample depth increased, which was in line with microstructural observations. The presence of the MgO peak at 42.9° 2θ indicated incomplete hydration, whereas the brucite peak at 38° 2θ was an indication of incomplete carbonation.

Figure 4.8 shows the XRD patterns of M10_H samples after 14 days of curing. The presence of nesquehonite, hydromagnesite and dypingite was seen at higher intensities when compared to the 1-day patterns due to the longer curing durations. The formation of these HMCs at higher contents was the main reason behind the increase in strength from 10 to 24 MPa. The brucite peak was not present after 14 days of curing, which was an indication of the complete carbonation of all the brucite that formed as a result of the hydration of MgO.

However, the presence of unhydrated MgO revealed incomplete hydration at the end of 14 days, which indicates that even higher strength results could have been obtained if the mix design and curing conditions were further optimized to enable higher hydration degrees.

The XRD patterns of P10_H samples after 14 days of curing are shown in Figure 4.9 for comparison purposes. The hydration (portlandite) and carbonation (calcite) products of PC were observed over the entire cross-section. The intensity of portlandite was relatively low even after 14 days of curing. The extent of carbonation for both the MgO and PC samples is dependent on many factors, some of which is mix design and curing conditions. As these samples were subjected to accelerated carbonation conditions under a high CO₂ concentration, the C-S-H and portlandite that formed due to the hydration of PC transformed into calcite, which was also observed in the XRD patterns. The intensity of the main calcite peak at 29.4° 2θ decreased towards the inner sections of the sample, which corresponded well with the MgO samples. This was because carbonation initially occurred on the sample surface and proceeded towards the inner cores as CO₂ diffused further into the sample.

Figure 4.7 XRD patterns of M10_H samples after 1 day of curing

(Q= quartz, M= MgO, B= brucite, H= hydromagnesite, D= dypingite, N= nesquehonite)

Figure 4.8 XRD patterns of M10_H samples after 14 days of curing

(Q= quartz, M= MgO, B= brucite, H= hydromagnesite, D= dypingite, N= nesquehonite)

Figure 4.9 XRD patterns of P10_H samples after 14 days curing

(Q= quartz, C= calcite, P= portlandite)

4.1.3.5 TG/DTA

The TGA results of MgO samples after 1 and 14 days of curing are shown in Figure 4.10 (a) and (b), respectively. According to the weight lost shown on the TGA curves, the decomposition steps of all samples can be divided into 3 main stages: (i) <250 °C due to the loss of unbound water and the water of crystallization of HMCs due to their dehydration, (ii) 250-500 °C due to the dehydroxylation of HMCs and the decomposition of any uncarbonated brucite, and (iii) >500 °C due to decarbonation process involving the decomposition of HMCs into MgO. The details of these stages are listed in Table 4.2.

The CO₂ content of each mix at different depths was calculated by using the weight loss obtained at >500 °C. The carbonation degree was then derived by dividing the actual amount of CO₂ absorbed during the curing process with the

maximum theoretical amount of CO_2 referring to the complete carbonation of the MgO used as a binder in the prepared mixes. According to this calculation, the carbonation degrees of M10_H samples after 1 day of curing were calculated as 32%, 23% and 20% at 0, 20 and 35 mm, respectively. A relatively small change was observed when the samples were cured for longer durations (i.e. 14 days). Small discrepancies in the TGA results of some samples were attributed to the sample preparation process as the original samples included a high percentage of aggregates that had to be broken down into powder in preparation for TGA. It is likely that the cement content within some of the prepared samples may be higher than the original mix composition.

The increase in the carbonation degree towards the exterior sections of the samples was because CO_2 was readily absorbed on the sample surfaces at initial stages of carbonation. This was in agreement with the earlier findings reported in this study, showing that even though it extends to the inner core of the samples, carbonation is limited at increased depths. This can be resolved with improved mix design where a continuous path for the diffusion of CO_2 into higher depths can be provided. Alternatively, the formation of the carbonate layer on the outer surface of the samples, which restricts further generation of carbonates, can be tackled with the introduction of certain additives. The solubility of CO_2 within the prepared formulations can also be increased via its dissolution under alkaline conditions.

Table 4.2 Different stages of the thermal decomposition of carbonated MgO samples

Temperature range (°C)	Peak temperature (°C)	Process	Reaction
< 250	80	Dehydration of HMCs	$Mg_a(CO_3)_b(OH)_c \cdot dH_2O \rightarrow Mg_a(CO_3)_b(OH)_c + dH_2O$
250-500	390	Dehydroxylation of HMCs & Decomposition of uncarbonated brucite	$Mg_a(CO_3)_b(OH)_c \rightarrow bMgCO_3 + (a-b)MgO + (c/2)H_2O$ $Mg(OH)_2 \rightarrow MgO + H_2O$
> 500	570	Decarbonation of HMCs	$MgCO_3 \rightarrow MgO + CO_2$

(a)

(b)

Figure 4.10 TGA curves of M10_H samples at different depths after (a) 1 day and (b) 14 days of curing

4.1.3.6 Microstructure

The SEM images of M10_H samples at different depths after 14 days of accelerated carbonation are shown in Figure 4.11. Clear formation of rosette-like dypingite/hydromagnesite was observed at all depths. Nesquehonite with a needle-like morphology co-existed with dypingite/hydromagnesite at greater depths (35 mm). This was a clear indication that carbonation proceeded to the inner core of the samples at the end of 14 days. Similar to MgO samples, the extent of carbonation at different depths of PC samples subjected to 14 days of curing is shown in Figure 4.12. The formation of calcite could be seen at all depths, whereas ettringite needles were observed towards the inner sections (20 mm).

A further investigation into the microstructure of MgO samples was performed by FESEM images taken at two magnifications after 1 and 14 days curing (Figure 4.13 and 4.14). At the end of 1-day curing (Figure 4.13), carbonation was observed only on the exterior (0 mm) of the sample, indicated by the formation of nesquehonite along with dypingite/hydromagnesite. No clear carbonation was spotted in the inner sections (20 and 35 mm) after 1 day of curing. However, a different scenario was observed in Figure 4.14, which depicted the progress of carbonation at 14 days. An extensive formation of dypingite/hydromagnesite with larger palettes than those formed at 1 day was observed on the exterior of the sample. The inner sections of the sample also indicated dense formation of dypingite/hydromagnesite, which co-existed with nesquehonite at the inner core (35 mm). The fibrous structures of these HMCs demonstrated interlocking properties, which led to a decrease in the porosity and an associated increase in density after carbonation. This increase in density, which was observed even in the inner core of the MgO samples after 14 days of curing, explains the high strengths obtained under accelerated carbonation. While HMCs dominated the microstructure of MgO samples, the formation of

calcite was observed in PC samples subjected to the same carbonation conditions (Figure 4.15).

Figure 4.11 SEM images of M10_H samples at different depths after 14 days of curing at: (a) 0 mm, (b) 20 mm and (c) 35 mm

Figure 4.12 SEM images of P10_H samples at different depths after 14 days of curing at: (a) 0 mm, (b) 20 mm and (c) 35 mm

Figure 4.13 FESEM images of M10_H samples at different depths after 1 day of curing at: (a)-(b) 0 mm, (c)-(d) 20 mm and (e)-(f) 35 mm

Figure 4.14 FESEM images of M10_H samples at different depths after 14 days of curing at: (a)-(b) 0 mm, (c)-(d) 20 mm and (e)-(f) 35 mm

Figure 4.15 FESEM images of P10_H samples at 0 mm at (a)-(b) 1 day and (c)-(d) 14 days

4.1.3.7 Carbonation depth

The carbonation process involves the conversion of alkaline hydration products into carbonate phases with lower pH values. The pH indicator (phenolphthalein) turns pink at a pH value of above 10 and becomes colorless when the pH reaches 8.2. Phenolphthalein can therefore be used to provide a general idea of the progress of carbonation at different depths. To enable this, samples were cut at three different depths (0, 20 and 35 mm) on which phenolphthalein was sprayed to indicate the extent of carbonation at each depth. Figure 4.16 and 4.17 show M10_H sample sections after 1 and 14 days of curing, respectively. The 14-day

samples indicated a lighter color than the dark pink observed in the 1-day samples, reflecting the decrease in the pH value with time as carbonation proceeded. For all the samples analyzed, the color faded on the exterior sections (0 mm), while the inner parts (20 and 35 mm) had darker colors. This darker shading was a reflection of limited carbonation, whose intensity decreased towards the inner core of the sample.

The pH values of the exterior MgO samples were measured by a pH meter and reported as 10.3 after 1 day of curing. A decrease in the pH to 9.8 was reported at the end of 14 days of curing. The pH values increased with sample depths and decreased with curing duration as the degree of carbonation increased. This was in line with the microstructural observations, also showing that carbonation started from the exterior surface of the samples and proceeded towards the inner parts with time. A similar carbonation trend was reported in the PC samples shown in Figure 4.18 and 4.19. Although a high degree of carbonation was observed on the exterior sections of PC samples indicated by the lack of change in color after the application of the pH indicator, the inner sections remained relatively uncarbonated. When compared to the M10_H samples, the extent of carbonation in P10_H samples was limited at increased depths, as shown by the darker shades obtained in the latter.

Figure 4.16 M10_H sample sections after 1 day of curing showing the different depths at (a) 0 mm, (b) 20 mm and (c) 35 mm

Figure 4.17 M10_H sample sections after 14 days of curing showing the different depths at (a) 0 mm, (b) 20 mm and (c) 35 mm

Figure 4.18 P10_H sample sections after 1 day of curing showing the different depths at (a) 0 mm, (b) 20 mm and (c) 35 mm

Figure 4.19 P10_H sample sections after 14 days of curing showing the different depths at (a) 0 mm, (b) 20 mm and (c) 35 mm

4.1.3.8 HCl acid test

The amount of CO₂ absorbed in M10_H and P10_H samples was measured by using the neutralization reaction between HCl acid and Mg- or Ca-based carbonates that formed at 1 and 14 days of curing. The results obtained at the end of this reaction are displayed in Figure 4.20. The generally higher carbonation degree results obtained by dissolving the samples in HCl acid than TGA measurements can be attributed to the high volatility of the acid and the heat emitted as a result of the rigorous reaction between the carbonated samples and HCl acid, which may have influenced the total weight loss recorded. However, since this is valid for all samples regardless of the cement binder used (MgO vs. PC), this method can still provide a comparison of the carbonation capability of each binder.

The carbonation degree increased from 1 to 14 days for all samples and was higher on the exterior sections (0 mm) than the inner parts (20 and 35 mm). This was because CO₂ could readily react with the cement matrix at the surface of the samples, thereby increasing the degree of carbonation. MgO samples achieved an average of 32% carbonation only after 1 day of curing. Curing for 14 days increased the degree of carbonation from 30% to 58% on the exterior of the MgO samples, whereas this value was limited to 28% for PC samples after 14 days of curing. The exterior of the samples (0 mm) indicated a much higher increase in carbonation degree at longer curing periods (from 1 to 14 days) when compared to the inner sections (20 and 35 mm) as the diffusion of CO₂ slowed down towards the core of the samples. This could be attributed to the formation of the initial carbonate network that reduced the connectivity of the originally available pore space, slowing down the diffusion rate of CO₂ with time. The maximum carbonation MgO samples achieved at the inner cores (35 mm) was 37% at 14 days, which was 51% higher than the carbonation degree

of the corresponding PC samples (18%). These results were a clear indication of the superior ability of MgO cement over PC in carbonating within porous applications. Since the formation of HMCs is the major contributor to mechanical performance, the strength of MgO samples increased with carbonation degree.

Figure 4.20 Carbonation degrees of M10_H and P10_H samples obtained by HCl acid test

4.1.4 Conclusions

This study investigates the strength and microstructural developments of a range of MgO cement concrete formulations subjected to 10% CO₂ curing for up to 28 days. Each mix composition included 5-10% cement and 85-90% natural aggregates at two different w/c ratios. The results were compared with PC concrete blocks. The fast strength development observed during the first 7 days stabilized afterwards, which was attributed to the decrease of CO₂ diffusivity within the reduced pore space that was filled up with hydration and carbonation

products. Carbonation initially occurred on the sample surfaces and gradually proceeded towards the inner cores. Carbonation degree decreased with an increase in sample depth and increased with curing duration. An abundant formation of HMCs such as hydromagnesite, dypingite and nesquehonite was observed along the cross-section of the MgO samples, resulting in a mechanical performance advantage over PC.

4.2 Study 2: Use of pre-conditioning

4.2.1 Introduction

Carbonation reaction kinetics involves the diffusion of CO₂ into the cement matrix and its interaction with the available hydration products. The main factors influencing the carbonation of concrete mixes in general are the diffusivity of CO₂ and its reactivity with concrete. Type and content of cement have an influence on both diffusivity and reactivity of CO₂, and water/cement ratio is related to the diffusivity of CO₂. The first study in 4.1 investigates the influence of these two factors on carbonation of MgO cement concrete. Some other factors such as temperature and relative humidity also control the carbonation of MgO, and are investigated by previous studies (Unluer & Al-Tabbaa, 2014; Liska, 2008). Pre-conditioning is a process where fan drying or oven drying was applied with relative humidity ranging from 50% to 98% and temperature ranging from 20 to 80 °C before normal curing. This method is designed to accelerate hydration/carbonation process and thus strength development of concrete.

Although pre-conditioning carbonation curing is proved to be an energy efficient method to accelerate strength development of PC (Morshed & Shao, 2013; Shi, He & Wu, 2012; Shi & Wu, 2008; Zhan, Xuan, Poon & Shi, 2016),

this method has not been used in carbonation of MgO cement before. The positive and negative effects of temperature and humidity on carbonation competed with each other and resulted in inconsistent results in previous studies. Besides, high temperature and high humidity have not been applied in pre-conditioning at the same time, and high humidity has potential to compensate the caking of concrete due to high temperature. It's interesting to know how the high temperature and humidity in pre-conditioning effect on strength development and carbonation of MgO cement concrete. This research investigates the effects of pre-conditioning involving elevated temperatures and humidity for different durations on the mechanical performance and microstructure development of MgO cement, in comparison to PC mixes. The findings proved that pre-conditioning is an effective way to enhance strength development by accelerating the hydration and carbonation process of MgO cement.

4.2.2 Mix design

A mix design containing 40% cement and 60% coarse aggregate by weight was applied in this study. The water to cement ratio of the samples was fixed at 0.6 for MgO cement samples to make sure the mix had an ideal workability. Before normal carbonation curing, MgO cement samples were placed in an environment chamber with elevated temperature between 40 to 60°C, and the humidity was fixed at 90%. The pre-conditioning process lasted for 1 to 2 days. After the pre-conditioning, all the MgO-containing samples were subjected to accelerated carbonation at 30 ± 2 °C and $80\pm 5\%$ RH under a CO₂ concentration of 10% for up to 56 days.

Table 4.3 Pre-conditioning used in this study

Sample	Temperature (°C)	Pre-conditioning duration
30	30	No pre-conditioning
40-1d 40-2d	40	1 and 2 days
50-1d 50-2d	50	1 and 2 days
60-1d 60-2d	60	1 and 2 days

4.2.3 Results and discussion

4.2.3.1 Compressive strength

After 3 to 56 days of CO₂ curing, concrete samples with different pre-conditioning were taken out from incubator and compressive strength was measured. Figure 4.21 shows the strength development of samples after 3 to 56 days of curing (including pre-conditioning and CO₂ curing). Before 7 days of curing, samples with or without pre-conditioning had similar strength results. Compared to control sample (30°C), samples with 40°C of pre-conditioning (40-1d, 40-2d) had no improvement in strength. Other samples with higher temperature of pre-conditioning at 50 and 60°C increased the strength by 2-4 MPa. This is because the strength gain of MgO cement is mainly based on the carbonation process. The short duration of carbonation in the early stage is not enough to obtain a high strength even there are more hydration products in the samples with pre-conditioning. Strength continued to increase from 7 days to 28 days of curing. The difference between samples with and without pre-

conditioning became more obvious. At 28 days of curing, samples with pre-conditioning at 60°C reached the highest strength at 46.8 MPa. The higher the temperature of pre-conditioning, the higher strength result. Samples exposed to higher temperatures during pre-conditioning had higher strength results. The strength of 60-2d and 50-2d samples was 16.4% and 22.8% higher than that of control samples, which demonstrates the advantage of pre-conditioning over normal curing samples. The duration of pre-conditioning also has influence on the strength development, pre-conditioning for longer duration at 2 days showed better strength results. While samples with pre-conditioning at 40°C stopped increasing after 28 days of curing, samples with higher temperature at 50 and 60°C still had a small increase. This can be explained by the higher hydration degree of the latter samples and thus more uncarbonated hydration products were available after 28 days of curing.

Figure 4.21 Compressive strength of samples under different pre-conditioning

4.2.3.2 Porosity

Figure 4.22 shows the porosities of all samples after 7, 28 and 56 days of curing with or without pre-conditioning. After 7 days of curing, MgO cement samples without preconditioning revealed a porosity of $\sim 4.2\%$, which was similar to samples subjected to pre-conditioning at 40°C . While samples subjected to higher temperature at 50 and 60°C had a lower porosity of $\sim 4.1\%$. This indicates high temperature pre-conditioning can enhance the hydration process of MgO cement and more hydration products form to make the microstructure denser. All samples experienced a decrease of porosity from 7 to 28 days of curing and the difference of porosity between samples with or without pre-conditioning became more obvious. The porosity of samples with pre-conditioning at 50 and 60°C decrease to 3.9% while other samples had a subtle decrease. The major carbonation products of MgO cement, HMCs, have a strong, fibrous, acicular or otherwise elongated nature via the interlocking effects occurring between the crystals, which makes the microstructure denser. Porosity stayed unchanged for control samples and samples with 40°C of pre-conditioning from 28 to 56 days of curing, which is related to the decreasing hydration and carbonation rate with curing time. There were insufficient hydration products available in those samples to produce carbonation products after 28 days. Porosity of samples subjected to high temperature pre-conditioning continued to decrease which indicates carbonation still proceeds in those samples after 28 days of curing. Those results are consistent with the strength development of MgO samples. Pre-conditioning at higher temperature of 50 and 60°C can enhance the hydration process and thus makes the microstructure densifies sooner. Higher hydration produces more carbonation products after 28 days and results in lower porosity at longer period.

Figure 4.22 Porosity of samples under different pre-conditioning

4.2.3.3 Isothermal calorimetry

Figure 4.23(a) and (b) show the heat flow and the cumulative heat of pastes over 48 h of hydration, respectively. Dissolution occurred a few minutes after mixing for all samples, which was reflected by the initial increase in the heat flow (Figure 4.23(a)). The dissolution of the control mix (30°C) indicated the lowest heat flow, while this process was more rapid for mixes with pre-conditioning at elevated temperature. The significantly higher and sharper exothermic peaks of samples with pre-conditioning when compared to the control mix confirmed that higher temperature can enhance the hydration of MgO. This trend became more obvious in samples with higher temperature treatment (50, 60°C). The cumulative heat curves in Figure 4.23(b) clearly indicated a higher degree of hydration achieved by samples with pre-conditioning at elevated temperature, whereas the control mix revealed the lowest heat. The degree of hydration increased with the increasing temperature. From the calorimetry results, samples subjected to temperature at 50 and 60°C had increased hydration rate of MgO cement while lower temperature at 40°C showed less effect, which is consistent with the strength results.

(a)

(b)

Figure 4.23 Isothermal calorimetry results of pastes showing the (a) heat flow and (b) cumulative heat.

4.2.3.4 Hydration degree by TGA

Figure 4.24 (b) shows the hydration degree of MgO paste samples at 1, 3 and 7 days at temperatures from 30 to 60°C. The results were obtained from TG/DTA (Figure 4.24(a)) on MgO paste samples described in 3.3.10. The increase of temperature resulted in an increase in the hydration degree of MgO at all durations. The elevated temperature played an important role at earlier stages (1-3 days), during which the hydration degree increased significantly with increasing temperature. When compared to 3 days, the effect of elevated temperature on increasing the hydration degree decreased at 7 days. Higher temperatures of pre-conditioning lead to greater hydration of the samples. Pre-conditioning at 50 and 60°C were identified as the most effective improvement of the hydration process. When compared to the control mix (30°C), whose hydration degree was limited to 43%, increasing temperature to 60°C enhanced the hydration process and increased the hydration degree to 65% at the end of 3 days. A similar trend was observed at 7 days, where the hydration degree of the control mix increased from 52% up to 69% when pre-conditioning was applied to samples. The results are consistent with the isothermal calorimetry results.

(a)

(b)

Figure 4.24 Hydration degree of MgO cement pastes under different temperatures

4.2.3.5 XRD

Figure 4.25 shows XRD patterns of MgO samples after 56 days of CO₂ curing with or without pre-conditioning. The presence of MgO, brucite, hydromagnesite and MgCO₃ can be found after 56 days of curing. The presence of the MgO peak at 43.5° 2θ indicated incomplete hydration, whereas the brucite

peak at 18.7° and $38^\circ 2\theta$ was an indication of incomplete carbonation. This finding means even if hydration and carbonation rate slowed down after 56 days of curing, the MgO cement still had potential for continuous hydration or carbonation. Hydromagnesite (PDF #025-0513) has its highest intensity peaks at $\sim 15.5^\circ$, 30.8° and $35.7^\circ 2\theta$, which confirmed the presence of hydromagnesite in the samples. Peaks of other HMCs such as dypingite and nesquehonite either overlapped with the main peaks of hydromagnesite or were too small to observe by XRD. By comparing MgO samples with and without pre-conditioning, the intensity of major hydromagnesite peaks were higher in the former, which explained the increasing strength after pre-conditioning. The elevated temperature and humidity of pre-conditioning accelerates the hydration process of MgO cement at the early stage and thus enhances carbonation during further curing.

The quantification of major phases within MgO samples, obtained via Rietveld analysis, is listed in Table 4.4. The results show that hydromagnesite content in 40°C of pre-conditioning stayed stable after 56 days of curing compared to the control mix. This suggests that 40°C had less effect on hydration process of MgO cement compared to higher temperature conditions. There was an increase in hydromagnesite after pre-conditioning at higher temperatures and an increase of 18.4% was found in 60-2d samples. Samples with longer pre-conditioning also showed a higher content of hydromagnesite after 56 days. A similar trend can be observed in brucite between control mix and pre-conditioning samples. Brucite increased around 16.5% in 60-2d samples after 56 days of curing compared to control mix. The higher temperature, the higher content of hydration and carbonation products in the MgO cement concrete, which indicated improved carbonation and strength development of MgO cement concrete.

Table 4.4 Quantification of major phases obtained by XRD-Rietveld analysis

Sample	MgO	Hydromagnesite	Brucite	Magnesite
30	24.4	40.7	32.7	2.2
40-1d	25.9	40.5	31.1	2.5
40-2d	23.7	40.8	32.6	2.9
50-1d	17.2	42.3	37.8	2.7
50-2d	14.6	46.5	36.5	2.4
60-1d	14	45.7	37.5	2.8
60-2d	11.3	48.2	38.1	2.4

Figure 4.25 XRD pattern of MgO cement under different pre-conditioning after 56 days of curing

(M: MgO, B: brucite, MC: magnesite, HM: hydromagnesite, N: nesquehonite)

4.2.3.6 TG/DTA

Figure 4.26 presents the TGA curve of MgO cement concrete samples after 56 days of curing with or without pre-conditioning. According to the endothermic peaks shown on the TGA curves, the decomposition steps of samples can be divided into 3 main stages (Table 4.5): (i) 40-300°C due to the loss of unbound water and the water of crystallization of HMCs (hydromagnesite), due to their dehydration, (ii) 300-500°C due to the decomposition of any uncarbonated brucite and the dehydroxylation of HMCs (hydromagnesite), and (iii) 500-800°C due to the decarbonation process of magnesite.

Table 4.6 presents the mass loss of MgO samples at different stages as previously listed. Since there is much overlap of different phases in each stage, it is difficult to quantitatively analyze mass loss of each stage. However, in general it is easy to find that the weight loss of 60-2d and 50-2d samples increased at temperatures of 40-300 and 300-500°C as well as the total mass loss after 2 months of curing. Higher temperature and duration of pre-conditioning results in a larger mass loss. The weight loss of 60-2d samples at 40-300°C which contributed to dehydration of HMCs increased about 13.8%. This indicates greater hydration and more carbonation products after curing, which agrees with XRD result. This trend is more obvious when temperature is higher.

Table 4.5 Different stages of the thermal decomposition of MgO samples

Temperature range (°C)	Process
< 100	Water evaporation
100-300	Dehydration of HMCs
300-500	Decomposition of uncarbonated brucite and HMCs
> 500	Decarbonation of magnesite

Table 4.6 Mass loss of samples obtained by TGA

Samples/ Mass loss (%)	<300°C	300-500°C	500-800°C	Total
30	13.7	24.6	2.4	40.7
40-1d	13.4	25.3	2.2	40.9
40-2d	13.8	26.5	2.1	42.4
50-1d	14.0	25.8	2.2	42.0
50-2d	15.2	26.8	2.4	45.6
60-1d	15.3	27.3	2.6	45.2
60-2d	15.6	28.0	2.7	46.3

Figure 4.26 TGA curves of MgO cement samples after 56 days of curing

4.2.3.7 Microstructure

The SEM images of samples with or without pre-conditioning after 56 days of curing are shown in Figure 4.27. The formation of rosette-like hydromagnesite is clearly observed, as confirmed earlier by XRD analysis. The fibrous structure of this HMC demonstrated interlocking properties, which are known to provide strength in MgO cement formulations. When compared to the control samples (30°C), increasing temperature of pre-conditioning led to an increase of hydromagnesite crystal size, which makes the microstructure denser in MgO cement. These observations were aligned with consistent with porosity results, highlighting the influence of pre-conditioning on the carbonation process of MgO cement.

Figure 4.27 SEM images of MgO cement samples after 56 days of curing: (a) 30, (b) 40-2d, (c) 50-2d, (d) 60-2d

4.2.4 Conclusions

This chapter investigated the effects of pre-conditioning with different temperatures and durations on the mechanical performance and microstructure development of MgO cement. Hydration degree under different pre-conditioning was studied by calorimetry and TGA of paste samples. Microstructural change and quantitative analysis of the composition of the samples under different pre-conditioning after 56 days of curing were studied by XRD, TGA and SEM. The findings of this study indicate the significant potential of pre-conditioning in achieving high strengths of MgO cement concrete within a few days. As demonstrated, hydration rate and degree and the morphology of the final carbonate phases can be enhanced through increasing the temperature and

duration of pre-conditioning, leading to significant improvements in mechanical performance.

5. PERFORMANCE AND MICROSTRUCTURE OF CARBONATED MGO CEMENT CONCRETE UNDER HIGH TEMPERATURES

This chapter describes the transformation of HMCs in MgO cement concrete under high temperatures of up to 550°C. The stability and transformation of hydrate and carbonate phases under elevated temperatures in different environments and their effect on the overall performance of carbonated MgO samples are reported. The changes in the strength of the prepared samples are evaluated by compressive strength testing at different durations. The identification and quantification of relevant phases are performed by XRD, TG/DTA and SEM. Links between carbonate content and morphology and sample performance are established at different temperatures ranging between 40 and 550 °C and exposure durations of up to 28 days under water, oven and furnace conditions. A combination of various microstructural analyses is used to discuss the relationship between the amount and properties of carbonate phases and strength development.

5.1 Introduction

Although the performance of carbonated MgO-based samples is mainly dependent on the formation and stability of HMCs, the changes in the properties of HMCs under high temperatures and their effect on the overall sample performance have not been studied in detail. Some of the frequently studied applications of MgO involve the partial or complete replacement of PC in

structural or non-structural components such as porous units, bricks and blocks (Unluer and Al-Tabbaa 2014, Vlasopoulos 2012, Unluer and Al-Tabbaa 2011, Liska 2009, Unluer 2012). These applications may involve the exposure of the finished product to increased temperatures. This is particularly critical as any variation in the exposure environment can influence the transformation pathway of HMCs and thereby the performance of the product. This study investigated the changes in the performance and microstructure of carbonated MgO samples subjected to 40-550°C under water, oven and furnace conditions. The stability and transformation of hydrate and carbonate phases under elevated temperatures in different environments and their effect on the overall performance of carbonated MgO samples demonstrate the key factors controlling the stability and transformation of phases formed by the hydration and carbonation of MgO. The findings not only facilitate understanding and controlling properties that affecting stability of the strength providing phases, but also provide a pathway for the development of a range of MgO-based construction products where the sequestration of CO₂ improves strength.

5.2 Mix design

Concrete mixes involving 10% MgO and 90% aggregates by mass (i.e. sand:gravel 10:7) were prepared for compressive strength testing and microstructural analysis via SEM. The water to cement (w/c) ratio was kept constant at 0.8, based on earlier findings (Pu & Unluer, 2016). Another set of paste samples were also prepared for microstructural analysis via XRD and TGA/DTA. The paste compositions did not include any aggregates to enable the extraction of carbonated paste from the samples without any contamination and to ensure accurate identification and quantification of the hydrate and carbonate phases via XRD and TGA/DTA.

The samples were demolded after 24 hours and subjected to accelerated carbonation curing (i.e. 10% CO₂ concentration, 30±2 °C temperature and 80±5% relative humidity) for 14 days, during which the majority of strength development takes place in MgO-based samples. Once curing was completed, the samples were subjected to three different conditions, whose details are listed in Table 5.1, to assess their performance in water (W), oven (O) and furnace (F) at different temperatures (40-550 °C) and durations (1 hour - 28 days).

Table 5.1 Curing conditions used in this study for the assessment of sample performance

Sample	Environment	Temperature (°C)	Duration
W40, W60, W80	Water tank	40, 60, 80	1 and 6 hours 1, 7, 14 and 28 days
O40, O60, O80	Oven	40, 60, 80	1 and 6 hours 1, 7, 14 and 28 days
F150, F250, F350, F450, F550	Furnace	150, 250, 350, 450, 550	1, 3 and 6 hours

5.3 Results and discussion

5.3.1 Compressive strength

Figure 5.1 shows compressive strengths of all concrete samples and the performance of each sample was compared to the control sample (C), whose

strength of 18.7 MPa after 14 days of carbonation curing, was taken as a benchmark.

The influence of water curing at 40, 60 and 80 °C for up to 28 days on strength development is indicated in Figure 5.1(a). While the change in strength was negligible at 40 °C up until 28 days, a slight decrease in strength was observed when the temperature increased to 60 and 80 °C. The strength reduction was more obvious at longer durations, gradually resulting in a 12% decline after 28 days of exposure to under water conditions at 80 °C, with respect to the initial strength (i.e. 16.4 vs. 18.7 MPa). A similar trend was observed in the strength of samples placed in oven at 40, 60 and 80 °C for up to 28 days. As shown in Figure 5.1(b), sample strength remained relatively stable at 40 °C, regardless of the exposure duration. Increasing the temperature to 60 and 80 °C resulted in a slight reduction in strength, which decreased further with exposure duration. The influence of these temperatures on the strength results was obvious at durations as short as 1 day, similar to those subjected to under water conditions. As the exposure duration increased to 28 days, a 13% reduction in strength was revealed under 80 °C, with respect to the initial strength (i.e. 16.3 vs. 18.7 MPa).

Even with the reductions observed after 28 days of exposure to 60 and 80 °C in water and oven, these samples maintained a strength that was still satisfactory for their use in several applications, such as masonry blocks (Sobolev & Amirjanov, 2010). This 12-13% change in strength at the higher temperature range could be associated with the formation of minor cracks and the decomposition of certain carbonate phases under elevated temperatures. For instance, some studies reported the decomposition of nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) into more stable carbonates at temperatures higher than 52 °C (Hopkinson 2012). Nesquehonite has an elongated morphology that provides a strong interlocking mechanism in carbonated MgO samples, enabling their

strength development. The transformation of nesquehonite into other carbonate phases such as hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), which is composed of round disk-like crystals, may result in a reduction in the binding capacity, thereby reducing the overall strength.

The third condition involved the exposure of samples to heating in a furnace from 150-550 °C for 1, 3 and 6 hours. The trend in strength reduction at different temperatures and durations is shown in Figure 5.1(c). Unlike water and oven conditions, the use of high temperatures in the furnace revealed immediate effects on sample strength, which was obvious even after an hour of exposure. The magnitude of the decline in performance was directly correlated with the exposure temperature and duration, causing a higher reduction as the temperature and duration increased. At the lower temperatures of 150 and 250 °C, the strength only reduced by up to 17% after 1 hour, during which a 73% reduction was observed at 550 °C. After 6 hours of exposure, the strength reduction revealed at different temperatures ranged between 34 and 84%, increasing with temperature.

This decline in strength was attributed to the changes in the amount and morphology of strength providing HMCs, which are known to start decomposing at temperatures as low as 52 °C (e.g. nesquehonite) (Hopkinson 2012) and around 255 °C (e.g. hydromagnesite) (Ballirano 2013; Botha & Strydom, 2001). The disturbance of the interconnected carbonate network provided by the dense formation of HMCs during the initial 14 days of curing, caused a notable reduction in performance. While this reduction was immediately apparent at the lower temperature range of 150 and 250 °C, increasing the temperature to 350 °C onwards had a profound effect on performance. A further increase in the temperature to ≥ 450 °C drained almost the entire strength of MgO samples, which was due to the decomposition of

even the more stable HMC phases, such as hydromagnesite, at these higher temperature ranges. These findings were in line with the literature (Ballirano 2013; Teir, Eloneva, Fogelholm & Zevenhoven, 2009; Vágvölgyi 2008), where the decomposition (i.e. involving the dehydration, dehydroxylation and decarbonation steps) of various HMCs were reported to take place at high temperatures similar to those used in this study. The decomposition of HMCs not only changes the initially dense microstructure but also results in the loss of structural integrity, thereby leading to a reduction in sample performance.

(a)

(b)

(c)

Figure 5.1 Compressive strength of samples subjected to (a) water, (b) oven and (c) furnace conditions

5.3.2 XRD

Figure 5.2 shows the XRD patterns of the main binder (MgO) and control sample (C), as well as selected samples subjected to water (W), oven (O) and furnace (F) conditions. The two main peaks of MgO at 42.9° and 62.4° 2θ , were accompanied with those of magnesite at 31.5° and 54.7° 2θ , as revealed in Figure 5.2(a), showing the incomplete decomposition of magnesite during the production of MgO. The main HMC phase observed in all carbonated samples was hydromagnesite (main peaks at 15.5° , 30.8° , and 35.7° 2θ), which formed as a result of the carbonation reaction. Regardless of the conditions they were subjected to, all samples, including the control sample, contained MgO, indicating incomplete hydration during the curing process. A similar observation was made about brucite (main peaks at 18.9° and 38.0° 2θ), whose presence was an indication of incomplete carbonation. The presence of residual MgO and brucite are a common occurrence in MgO-based formulations subjected to even longer durations (≥ 28 days) of carbonation, as reported in previous studies (Dung & Unluer, 2016, 2017a, 2017b, 2017c).

When compared to the control sample, there was an insignificant change in the presence of hydromagnesite amongst samples subjected to water and oven conditions at different temperatures and durations. This trend was in line with the compressive strength results, which only revealed a small decrease in strength even under 80°C . A different scenario was observed in samples subjected to heating in the furnace, whose XRD patterns (Figure 5.2(b)). While hydromagnesite could still be identified in samples subjected to the lower temperature range of $150\text{--}250^\circ\text{C}$, increasing the temperature to 350°C onwards reduced the intensities of the major hydromagnesite peaks in all samples. Going from 1 to 6 hours of exposure under 350°C led to an obvious decline in the intensity of hydromagnesite, which was not readily detected in any samples subjected to temperatures of $> 350^\circ\text{C}$. The reduction and eventual

disappearance of hydromagnesite was accompanied with a simultaneous increase in the intensity of the MgO peak, which could be visibly seen at the higher temperature range. These changes in composition was an indication of the decomposition of hydromagnesite to the original binder phase (MgO) as the exposure temperature increased, explaining the deterioration of sample performance observed earlier (Figure 5.1).

The quantities of the major phases within selected samples, obtained via Rietveld analysis, are listed in Table 5.2. As revealed by the XRD patterns, the presence of undecomposed magnesite, adopted from the original binder (MgO), was relatively stable at around 8-10% in all samples. The exposure conditions mainly affected the content of MgO, brucite and hydromagnesite. Within the samples subjected to water and oven conditions, a slight decrease in the MgO content and an associated increase in the brucite content was observed with time (i.e. going from 1 hour to 14 days of exposure) when compared to the control sample, which was an indication of the continuation of the hydration reaction over time. In addition to increased brucite contents, an obvious increase in the hydromagnesite contents of these samples was observed in comparison to the control. These changes in the phase contents could be associated with the use of elevated temperatures (i.e. 60-80 °C) that stimulated the dissolution of MgO within the pore solution and its reaction with the other dissolved phases, even after the initial curing period.

The hydromagnesite content was relatively constant amongst all the W and O samples subjected to different temperatures (60 and 80 °C) for different durations (1 hour and 14 days), which could explain their rather stable strengths. This could be an indication that any reduction in strength observed in these samples, albeit small, could be due to the formation of minor cracks under elevated temperatures, instead of major phase changes. Alternatively, subjecting

the samples to furnace conditions led to a visible change in the contents of the major phases at ≥ 350 °C. While a decrease in MgO and an increase in brucite contents in comparison to those of the control sample was revealed within samples subjected to the lower temperature ranges, similar to those seen in W and O samples, this trend reversed as the temperature was raised to 350 °C and higher. A clear reduction in the carbonate (i.e. hydromagnesite and magnesite) and brucite contents, accompanied with an increase in the MgO content, was observed at the higher temperature ranges. Those subjected to 550 °C for 6 hours (F550-6h) revealed a similar MgO content as the original binder composition, which was an indication of the complete decomposition of all carbonate phases. These findings were in line with previous studies (Ballirano 2013; Botha & Strydom, 2001; Teir 2009), where similar trends regarding the decomposition of hydromagnesite at > 255 °C were reported, explaining the decline in strength revealed by the F samples.

(a)

(b)

Figure 5.2 XRD patterns of (a) MgO, control and selected samples subjected to water and oven conditions; and (b) selected samples subjected to furnace conditions (M: MgO, MC: Magnesite, B: Brucite, H: Hydromagnesite)

Table 5.2 Mass percentage quantities of the major phases obtained by XRD-Rietveld analysis

Sample	MgO	Brucite	Magnesite	Hydromagnesite
MgO powder	71.2	19.6	9.2	-
C	26.4	43.7	9.6	20.3
W60-1h	20.1	44.9	9.1	25.9
W60-14d	19.0	46.4	10.3	24.3
O60-1h	21.5	44.2	9.7	24.6
O60-14d	19.7	46.7	9.1	24.5
O80-1h	20.4	44.2	9.9	25.5
O80-14d	20.7	45.7	9.6	24.0
F150-1h	21.7	46.8	9.7	21.8
F150-6h	20.3	49.4	8.8	21.5
F350-1h	23.2	50.6	9.4	16.8
F350-6h	27.9	53.0	7.6	11.5
F550-1h	59.9	35.6	0.8	3.7
F550-6h	69.3	28.0	0.4	2.3

5.3.3 TG/DTA

The mass loss and heat flow data of selected samples subjected to water, oven and furnace conditions under various temperature and duration combinations, as well as the control sample, are presented in Figure 5.3. The three main decomposition steps observed in the presented data were in agreement with the pervious literature (Ballirano 2010a; Frost, Bahfenne, Graham & Martens, 2008; Frost & Palmer, 2011; Hollingbery & Hull, 2010; Jauffret, Morrison & Glasser, 2015) and identified as:

40-300 °C: Dehydration of water bonded to hydromagnesite (Equation 5.1)

300-500 °C: Dehydroxylation of hydromagnesite (Equation 5.2) and decomposition of uncarbonated brucite (Equation 5.3)

500-800 °C: Decarbonation of all carbonate phases (Equation 5.4)

The locations of the endothermic peaks corresponding to each decomposition reaction are revealed in Figure 5.3. Accordingly, the two main endothermic peaks due to the dehydration of loose water and water bonded to hydromagnesite were observed at around 120 and 230 °C, respectively. A strong endothermic peak responsible for the decomposition of uncarbonated brucite was observed at ~370 °C. Following this was a smaller peak at ~440 °C due to the dehydroxylation of hydromagnesite. The decarbonation of all carbonate phases (e.g. hydromagnesite that formed as a result of the carbonation reaction and undecomposed magnesite present in the original binder), which took place at temperatures higher than 500 °C, was accompanied with an endothermic peak at ~560 °C. While this particular trend was seen in all samples subjected to water, oven and furnace conditions until 350 °C, the disappearance of the carbonate peaks was observed as the exposure temperature increased to > 350 °C. Alternatively, a smaller peak at ~350 °C referring to the decomposition of brucite was seen in samples F550-1h and F550-6h, instead of all the usual peaks observed in other samples.

The mass loss obtained from the decomposition of hydrate and carbonate phases within each sample at different steps, along with the total mass loss, are listed in Table 5.3. When the three temperature ranges were compared, a higher mass loss between 300 and 500 °C was observed. This mass loss was attributed to the dehydroxylation of hydromagnesite and the decomposition of uncarbonated brucite. Within the initial temperature range of 40-300 °C, mass loss values ranging between 8-14% were revealed amongst the control sample and samples subjected to water and oven conditions. The amount of mass loss within this range generally decreased with increased exposure temperature and duration. A further decrease in these mass loss values were observed in the samples exposed to high temperatures in the furnace, which was due to the evaporation of water under the furnace conditions.

In line with the phase quantifications obtained by XRD, the control, W, O and some of the F samples (i.e. those subjected to < 550 °C) revealed similar mass loss values of 22.8-27.9% in the 300-500 °C range, which was associated with the presence of brucite as well as hydromagnesite. A clear reduction in mass loss was observed in F-550 samples, resulting in values as low as 11%. These decreased mass losses were an indication of the reduced brucite and hydromagnesite contents at higher exposure temperatures, as also shown earlier by the XRD results. However, it must be noted that even in F550-6h samples (i.e. subjected to heating in the furnace under 550 °C for 6 hours), the occurrence of mass loss, albeit small, was due to the presence of undecomposed hydrate and carbonate phases within the sample structure. Considering the low mass loss (~3%) demonstrated in the subsequent temperature range of 500-800 °C due to the decomposition of carbonates within these samples, a majority of the mass loss between 300-500 °C was associated with the presence of brucite as opposed to carbonates, as also revealed earlier in Table 5.2. As the sole presence of brucite within MgO-based formulations does not have a significant contribution

to strength gain, when coupled with the drying-related cracking, F550 samples were not able to maintain their initial strengths under the high temperatures they were exposed to.

Differing from F550 samples, all other samples led to mass losses within the narrow range of 12.4-14.6% at 500-800 °C, indicating the stability of carbonate phases up until 350 °C. A similar trend was observed in the total mass loss values, where the values demonstrated by W, O, F150 and F350 samples (43.3-50.5%) remained comparable to the control sample (51.1%). An obvious reduction in the total mass loss to 18.7% was observed when the temperature was raised to 550 °C. These outcomes were in agreement with the strength results, which revealed a notable decline in sample performance when the exposure temperatures were increased to > 350 °C.

(a)

(b)

Figure 5.3 Mass loss and heat flow curves of samples subjected to (a) water and oven and (b) furnace conditions

Table 5.3 Mass loss of samples at different temperature ranges obtained by TGA

Sample	Mass loss (%)			Total
	40-300°C	300-500 °C	500-800 °C	
C	12.5	25.9	12.7	51.1
W60-1h	13.2	24.9	12.4	50.5
W60-14d	8.0	24.3	13.3	45.6
O60-1h	14.0	22.8	12.5	49.3
O60-14d	8.1	26.1	13.2	47.4
O80-1h	9.4	23.7	13.5	46.6
O80-14d	8.8	27.9	12.8	49.5
F150-1h	7.5	24.5	12.9	44.9
F150-6h	7.2	26.0	13.4	46.6
F350-1h	3.1	25.6	14.6	43.3
F350-6h	5.2	25.7	14.3	45.2
F550-1h	4.6	14.3	2.7	21.6
F550-6h	4.7	11.0	3.0	18.7

5.3.4 Microstructure

The microstructures of the control sample and selected samples subjected to water, oven and furnace conditions are shown in Figure 5.4. Other than MgO and brucite, the rosette-like formation of hydromagnesite was observed in most samples. Samples subjected to temperatures of up to 150 °C revealed similar microstructures with the control sample. Within these samples, a widespread network of hydromagnesite clusters, along with other uncarbonated phases, were detected.

When compared to the control, W and O samples; exposing the samples to high temperature conditions in the furnace led to microstructures composed of loosely arranged carbonate clusters, as opposed to the dense networks observed at lower temperatures. A further increase in the temperature to 350 °C and

higher revealed microstructures with a scarce formation of carbonates. In addition to a decline in their amount, the carbonates observed at these elevated temperatures were composed of smaller crystals, which was attributed to the changes in their structures. The reduction in the content and size of carbonates at 350 °C was followed by their disappearance at 550 °C. Differing from others, F550 samples demonstrated microstructures composed of uncarbonated brucite and MgO, without any major sign of carbonate phases. These observations were aligned with the strength and phase quantification results reported earlier, highlighting the influence of different exposure conditions on sample structure and associated performance.

Figure 5.4 SEM images of samples (a) control, (b) W60-1h, (c) W60-14d, (d) O80-1h, (e) O80-14d, (f) F150-1h, (g) F150-6h, (h) F350-1h, (i) F350-6h, (j) F550-1h, (k) F550-6h

5.4 Conclusions

This study investigated the changes in the performance and microstructure of carbonated MgO samples subjected to 40-550°C under water, oven and furnace conditions. While sample strength remained relatively stable until 80°C, an obvious reduction was observed under higher temperatures. This performance decline was attributed to the changes in the content and morphology of strength providing carbonate phases (hydromagnesite). Phase quantification results revealed lower contents of hydromagnesite with smaller crystal sizes at $\geq 150^\circ\text{C}$. The decarbonation of hydromagnesite, followed by dehydration of brucite to MgO at higher temperatures of 550°C, revealed the relationship between the stability of major phases and sample performance.

6. DURABILITY OF CARBONATED MGO CEMENT CONCRETE CONTAINING FLY ASH AND GROUND GRANULATED BLAST-FURNACE SLAG

This chapter investigates the durability of carbonated MgO cement concrete containing pulverized fly ash (PFA) and ground granulated blast-furnace slag (GGBS) under harsh conditions. Samples containing MgO cement are subjected to accelerated carbonation at 30 ± 2 °C, $80\pm 5\%$ RH and 10% CO₂ concentration for 28 days. PC samples are cured under 30 ± 2 °C, $80\pm 5\%$ RH and ambient CO₂. After 28 days of curing, samples are subjected to four different conditions involving: (i) 10% sodium chloride solution, (ii) 10% sodium sulfate solution, (iii) freeze-thaw cycling in 10% sodium chloride solution, and (iv) seawater for up to 6 months. The performance of these samples is compared to PC-based concrete samples that are subjected to the same conditions. This is followed by an assessment of their performance via porosity, pH and compressive strength measurements at different durations. The formation of different phases within MgO cement mixes is investigated via XRD, TGA and SEM.

6.1 Introduction

Concrete structures exposed to harsh environments usually suffer from physical and chemical deterioration. Durability is crucial for concrete to retain its mechanical performance during its lifetime. Although there are a lot of studies on performance of PC concrete blocks under harsh environments (Moffatt & Thomas 2018; Valipour, Shekarchi & Arezoumandi 2017; Wang, An, Yu, Han

& Ji 2017; Martin-Morales, Cuenca-Moyano, Valverde-Espinoza & Valverde-Palacios 2017; Muhammad, Zaki, Mohammed, Fahad & Mohammed 2016; Yoshida, Maeno, Iiboshi & Araki 2018; Chaipanich & Chindaprasirt 2015), few studies investigate the long-term performance of carbonated MgO cement samples with and without the use of SCMs under various aggressive environments concrete samples are exposed to in practical applications. This study aims to investigate the performance of MgO-PFA and MgO-GGBS based mixes under different environments, whose influence on strength development was evaluated via a comparison of these mixes to PC-based concrete samples subjected to the same environments. The prepared samples were subjected to 4 different chemical attacks for up to 6 months. Overall, MgO cement concrete with supplementary cementitious materials such as pulverized fly ash (PFA) and ground granulated blast-furnace slag (GGBS) was demonstrated to have better durability over PC concrete in chloride, sulfate attack and freeze-thaw cycling.

6.2 Mix design

Four mix designs containing 40% binder and 60% coarse aggregates by mass were prepared in this study. These concrete compositions did not include any fine aggregates to enable the extraction of carbonated paste from the concrete samples without any contamination and to ensure accurate quantification of the hydrate and carbonate phases via XRD and TGA. The cement binder was composed of: (i) MgO cement alone (M40 mixes), (ii) 50% MgO cement and 50% PFA (M20F20 mixes), (iii) 50% MgO cement and 50% GGBS (M20G20 mixes), and (iv) PC alone (P40 mixes). The water to binder (w/b) ratio of each mix was determined according to the standard consistencies of each binder component, resulting in mixes that achieved full compaction with similar workability levels. The detailed mix compositions are presented in Table 6.1.

Once the mixing process was completed, samples were cast in 50x50x50 mm cubic molds, consolidated by using a vibrating table and trowel finished, after which they were kept in sealed conditions for 24 hours until demolding. Samples containing MgO cement (M40, M20F20 and M20G20) were subjected to accelerated carbonation at 30 ± 2 °C, $80\pm 5\%$ RH and 10% CO₂ concentration for 28 days. PC samples (P40) were cured under 30 ± 2 °C, $80\pm 5\%$ RH and ambient CO₂. After 28 days of curing, samples were subjected to four different conditions involving: (i) 10% sodium chloride (SC) solution, (ii) 10% sodium sulfate (SS) solution, (iii) freeze-thaw (FT) cycling in 10% sodium chloride solution, and (iv) seawater (SW). The exposure duration ranged between 1 to 6 months, during which the mechanical performance and microstructural development of samples were continuously investigated.

Table 6.1 Mix compositions investigated in this study.

Sample	Content (%)					w/b ratio
	MgO	PFA	GGBS	PC	Gravel	
M40	40	0	0	0	60	0.60
M20F20	20	20	0	0		0.45
M20G20	20	0	20	0		0.45
P40	0	0	0	40		0.35

6.3 Results and discussion

6.3.1 Compressive strength

The compressive strength of all samples before durability testing (at 28 days) and at different durations (1, 3 and 6 months) of exposure are shown in Figure 6.1. Amongst all the prepared samples, M40 demonstrated the highest strengths at all times, regardless of the exposure condition it was subjected to. The highest initial (28 day) strength of M40, 41.4 MPa, was associated with the formation

of HMCs during carbonation curing under 10% CO₂. Alternatively, samples containing PC as their main binder component, P40, led to strengths of 36.7 MPa, which was based on the progress of hydration and the formation of hydrate phases such as C-S-H and Ca(OH)₂. The inclusion of PFA and GGBS in MgO cement mixes led to lower initial strengths of 39 and 33 MPa, respectively. This reduction in strength was due to the lower MgO content within samples M20F20 and M20G20, which led to lower HMC contents and thus lower strength results. The lower strengths of these samples could also be associated with the filler effect of PFA and GGBS, which decreased the initial porosity, thereby slowing down the diffusion of CO₂ during the curing process.

Regardless of their compositions, all samples demonstrated a reduction in strength as the duration of exposure to aggressive environments increased. A decrease of up to ~9% was observed after 1 month of exposure, which was higher at ~18% after 6 months. Amongst all the conditions used, sodium sulfate (SS) exposure led to the most obvious reduction (10.7-17.8%) in strength at 6 months, whereas seawater had the lowest influence (5.8-6.9%) on strength results. The reduction in the strength of M40 samples exposed to SC and SS conditions could be related to the potential formation of new phases (e.g. magnesium chloride and magnesium sulfate) via the reaction of Mg²⁺ and Cl⁻/SO₄²⁻, which did not contribute to strength as the carbonate phases. When the different compositions were compared, it was observed that M40 samples, containing only MgO for their binder component, revealed the highest strengths under all exposure conditions, followed by M20F20, P40 and M20G20 samples. The higher strengths of M40 could be associated with the stability of the carbonate phases as well as the low solubilities of Mg-hydrates and carbonates under aggressive environments, when compared to Ca-based hydrate phases in P40.

The use of PFA and GGBS in carbonated MgO cement mixes was generally favorable in terms of their lower degrees of strength reduction when compared to M40 samples, as can be observed in Table 6.2, where the percentage reduction in the strengths of all samples under each condition are listed at different durations. With the partial replacement of MgO with PFA and GGBS, the strength reduction in each condition reduced by about 2-4% in comparison to M40 samples, which could be associated with the filler effect of PFA and GGBS. Under SS and FT conditions, samples containing MgO cement (M40, M20F20, M20G20) revealed a better resistance to chemical attack than samples containing PC (P40), as evident by the lower strength reduction of the former. The variations in the performance of each sample were linked with the stability of different phases that formed in each mix design under different conditions.

(a)

(b)

(c)

(d)

Figure 6.1 Compressive strength of samples subjected to (a) SC, (b) SS, (c) FT and (d) SW conditions

Table 6.2 Percentage reduction in strength of all samples at different durations under each durability condition.

Sample	SC			SS			FT			SW		
	1 mon.	3 mon.	6 mon.	1 mon.	3 mon.	6 mon.	1 mon.	3 mon.	6 mon.	1 mon.	3 mon.	6 mon.
M40	4.8	7.6	10.9	6.1	10.1	12.8	5.7	9.1	12.7	0.6	4.3	6.9
M20F20	3.3	5.1	6.7	4.5	7.9	10.7	5.1	9.5	11.1	0.5	2.6	6.1
M20G20	4.5	5.9	8.7	5.4	9.4	11.4	4.3	10.4	11.9	0.1	3.7	5.8
P40	3.1	4.9	5.8	8.9	14.4	17.8	8.7	12.5	16.7	0.5	2.0	5.8

6.3.2 Porosity

Figure 6.2 shows the porosities of all samples before and after exposure to different conditions. After 28 days of curing (i.e. before exposure), M40 samples revealed a porosity of ~4.2%, which was similar with other samples. The initial 28-day porosities of all samples ranged between 4.1-4.3%, during which the inclusion of PFA and GGBS in samples M20F20 and M20G20 led to slightly lower porosities. This reduction in porosity, which was more pronounced for M20G20 samples, was associated with the formation of hydrate phases such as M-S-H and hydrotalcite due to the reaction between MgO cement and PFA/GGBS, as well as the small-size of PFA and GGBS particles that filled in the gaps between MgO cement agglomerates, increasing the density of the prepared samples. After being exposed to different conditions, all samples experienced an increase in porosity, which was more obvious over time. After 6 months of exposure, M40 samples revealed a porosity of 4.35- 4.85%, while the porosity of P40 samples ranged from 4.51% to 4.95%. Under most exposure conditions (SS, FT and SW), samples containing MgO cement revealed lower porosities than those with PC. The inclusion of PFA and GGBS led to samples with lower porosities at all times, explaining the generally lower percentage

reduction in strength achieved by samples M20F20 and M20G20 when compared to M40 and P40 under different conditions.

The percentage increase in the porosities of all samples at different durations under each durability condition is listed in Table 6.3. M40 samples revealed lower increases in porosity than P40 samples under SS and FT conditions, which was in line with their lower percentage reduction in strength under these conditions. The inclusion of PFA and GGBS presented an advantage by reducing the initial porosity and thereby enabling lower increases in porosity than MgO cement samples under different conditions, which increased the resistance of samples M20F20 and M20G20 to chemical penetration. Similar to the strength results, amongst all the conditions studied, SS and FT led to the highest change in the porosities of all samples, which increased by up to 13.8% after 6 months of exposure. This was followed by chloride attack (SC), which led to a 4.3-9.1% increase in the porosities of all samples. Exposure to seawater (SW) was the least detrimental amongst all conditions, increasing the porosity by 2.7-3.1% after 6 months. While most conditions (SS, SC and SW) purely involved the ingress of ions in the pore system and the stability of hydrate/carbonate phases under the changing environment, exposure to FT increased sample porosity not only via chemical attack but also via dimensional changes due to the expansion experienced at different temperatures. Overall, there was a direct relationship between the strength and porosity results of all samples, in which a higher increase in porosity corresponded to a higher reduction in strength. This link was mainly due to the increase in the pore space of each sample with time of exposure, which increased vulnerability to chemical attack and thereby reduced strength.

(a)

(b)

(c)

(d)

Figure 6.2 Porosity of samples subjected to (a) SC, (b) SS, (c) FT and (d) SW conditions

Table 6.3 Percentage increase in porosity of all samples at different durations under each durability condition.

Sample	SC			SS			FT			SW		
	1 mon.	3 mon.	6 mon.	1 mon.	3 mon.	6 mon.	1 mon.	3 mon.	6 mon.	1 mon.	3 mon.	6 mon.
M40	2.0	4.9	8.1	6.1	12.1	12.8	5.7	9.1	12.7	0	1.2	3.1
M20F20	1.7	3.8	6.2	4.5	7.9	10.7	5.1	9.5	11.1	0	0	3.4
M20G20	2.6	3.8	7.6	4.2	10.4	12.1	4.3	10.4	11.9	0.1	2.1	2.7
P40	1.5	3.1	4.3	5.9	10.4	13.8	5.7	9.7	13.7	0.2	2.0	2.8

6.3.3 Chloride penetration

The average chloride penetration depth was obtained by determining the chloride-contaminated zone on the cross-sectional areas of each sample. The progress of penetration over time in all samples is shown in Figure 6.3, where the area occupied by the light-colored region continuously increased from 1 to 6 months of exposure, indicating the penetration of chloride into the interior sections with time. Measurements were taken to reveal the results listed in Table 6.4, which indicate the chloride penetration depth of all samples subjected to SC environment for 1, 3 and 6 months. An increase in the penetration depth with time was observed in all samples, which was consistent with the performance and microstructural observations presented earlier. The depth of penetration was lower in samples M20F20 and M20G20 due to the improved resistance of these samples in the presence of PFA and GGBS, respectively. In line with the strength results (Figure 6.1), when compared to samples containing PC (P40), MgO-based samples (M40) revealed lower depths of penetration at all durations.

The changes in chloride concentration at different depths within M40 samples subjected to SC, FT and SW conditions are shown in Figure 6.4, where the chloride concentration at a depth of 1-4 mm from the sample surface was

displayed (i.e. 4 mm is sufficient to obtain a relatively comprehensive chloride penetration profile of each sample). Amongst the three exposure environments, those subjected to FT revealed the highest chloride concentration due to the significant increase in porosity (Table 6.3) via the large temperature differences used under this condition. These higher porosities increased the samples' vulnerability for the ingress of ions, which became more pronounced as the duration of exposure increased. Alternatively, samples subjected to SW revealed the lowest chloride concentrations at all depths, which was in line with the limited increase in porosity as well as the lower chloride concentration in seawater when compared to the solutions used in SC and FT conditions. The changes in the concentration of chloride throughout sample depth over the exposure duration were also in line with the strength results, where an increase in the Cl^- concentration led to lower strengths.

A further comparison of chloride concentration over sample depth for different samples subjected to SC exposure for 6 months are provided in Figure 6.5. While there were some variations in the chloride concentration towards the sample exteriors, the concentration decreased and led to similar values for all samples at higher depths. The slightly lower concentration of chloride observed within M40 samples in comparison to P40 samples could reveal the lower ingress of the ions within the former in line with their lower initial porosity, albeit their higher decrease in strength and increase in porosity. In line with the strength (Table 6.2) and porosity (Table 6.3) measurements, the inclusion of PFA and GGBS in MgO cement formulations led to a reduction in the concentration of chloride entering the sample pore structure, which was associated with the densification of the microstructure via the inclusion of these SCMs. These outcomes were consistent with the findings of previous studies (Chindaprasirt, Chotithanorn, Cao & Sirivivatnanon, 2007; Papadakis, 2000;

Yazıcı, 2008), which revealed the benefits of SCMs in improving the durability of concrete by reducing chloride penetration.

Sample	1 month	3 months	6 months
M40
M20F20
M20G20
P40

Figure 6.3 Progress of chloride penetration over time in samples subjected to SC exposure

(a)

(b)

(c)

Figure 6.4 Chloride concentration over sample depth within samples M40 exposed to SC, FT and SW conditions for (a) 1, (b) 3 and (c) 6 months

Figure 6.5 Chloride concentration over sample depth within all samples subjected to SC exposure for 6 months

Table 6.4 The average chloride penetration depth (X_d , mm) in samples subjected to SC exposure.

Sample	Duration (months)		
	1	3	6
M40	4.1	8.2	15.6
M20F20	3.4	7.8	13.7
M20G20	3.6	7.4	14.2
P40	4.3	11.6	17.4

6.3.4 XRD

Figure 6.6 shows the XRD pattern of samples containing MgO cement (M40, M20F20 and M20G20) after 28 days of curing and 1 and 6 months of exposure to different conditions. The presence of MgO, brucite and hydromagnesite was found after 28 days of curing. The presence of the MgO peak at 42.9° 2θ indicated its incomplete hydration, whereas the brucite peaks at 18.7° and 38.0° 2θ were an indication of incomplete carbonation. The main HMC peak observed in all samples was hydromagnesite (PDF #025-0513), which had its highest

intensity peaks at $\sim 15.5^\circ$ and 30.8° 2θ . Peaks of other HMCs such as dypingite and nesquehonite either overlapped with the main peaks of hydromagnesite or were too small to be observed in the XRD spectrum.

As can be seen in Figure 6.6(a), a decline in the intensity of major hydromagnesite peaks were observed in M40 samples as the time of exposure increased. This was an indication of the reduction in the amount of hydromagnesite under chemical attack, the main source of strength in carbonated MgO cement concrete formulations. Along with hydromagnesite, there was a relatively smaller increase in the MgO and brucite peaks. These observations were confirmed with the quantification of major phases within M40 samples obtained via Rietveld analysis (Table 6.5). When compared to the initial 28-day values, increases in the MgO (i.e. 3-12% after 6 months) and brucite (i.e. 4-17% after 6 months) peaks were accompanied with a reduction of up to 26% in the hydromagnesite content in all samples after 6 months of exposure. These changes in the phase contents were most obvious under SS condition, which could be due to the instability of HMCs and leaching of ions when the pH value was under 10 (i.e. the pH of initial NaCl and NaSO₄ solutions were around 8) (Liska & Al-Tabbaa, 2012; Sato, Akita, Hamadate & Fukushi, 2001). This was supported by the ICP-OES measurements presented in Table 6.6, where an increase in the Mg content to 32.6 and 100.9 mg/L was observed in SC and SS solutions after 6 months of exposure, respectively. Similarly, as shown in Table 6.7, the decline in the chloride and sulfate contents after the durability test indicated the possible participation of these ions in the reaction between the cement paste and the respective solutions. The increase in the MgO and brucite contents and the corresponding decrease in the hydromagnesite content could reveal the conversion of HMCs into Mg(OH)₂ and MgO under aggressive environments.

The XRD patterns of M20F20 (Figure 6.6(b)) and M20G20 (Figure 6.6(c)) samples indicated the presence of hydromagnesite along with hydrate phases hydrotalcite and brucite, as well as unreacted MgO. Differing from M40 samples, the XRD patterns of M20F20 samples shown in Figure 6.6(b) indicated the existence of mullite, which is present in PFA. While the presence of M-S-H was also expected, it was hard to identify in the XRD patterns due to its amorphous nature. The intensities of the brucite peaks were lower than those observed in M40 samples, which was associated with the lower MgO content and the slower hydration in the presence of PFA/GGBS. A similar pattern in the peak intensities was observed as those in M40 samples, where a decline in the hydromagnesite content was recorded after 6 months of exposure. However, this change was less obvious as the initial intensity of the hydromagnesite peaks in these samples was lower than those seen in M40 samples. Unlike hydromagnesite, the presence of hydrotalcite could be observed even after 6 months of chemical attack, which could explain the lower strength reduction achieved by these samples over time of exposure.

Figure 6.6 XRD patterns of (a) M40, (b) M20F20 and (c) M20G20 samples

(M: MgO, B: brucite, HM: hydromagnesite, HT: hydrotalcite, Mu: mullite, Q: quartz)

Table 6.5 Quantification of major phases in M40 samples obtained by XRD-Rietveld analysis.

Sample	Duration (months)	Phase (%)			
		MgO	Brucite	Hydromagnesite	Magnesite
M40	Initial (28 days)	29.1	31.8	37.4	1.7
M40-SC		28.7	32.4	36.8	2.1
M40-SS	1	30.2	32.3	35.1	2.4
M40-FT		29.8	31.7	36.6	1.9
M40-SW		29.0	31.7	37.2	2.1
M40-SC		30.1	33.2	34.5	2.2
M40-SS	6	32.5	37.3	27.6	2.6
M40-FT		31.8	32.2	34.3	1.7
M40-SW		30.1	32.5	35.6	1.8

Table 6.6 The ion content (mg/L) of SC and SS solutions after 6 months of exposure, as obtained by ICP-OES.

Ion	Solution	
	SC	SS
Na	Saturated	Saturated
Ca	1.5	6.8
Mg	32.6	100.9
Al	0.07	0.09

Table 6.7 The ion content (mg/L) of SC and SS solutions at different durations, as obtained by IC.

Ion	Solution			
	SC		SS	
	Initial	6 months	Initial	6 months
Cl	197.2	88.7	-	-
SO ₄	-	-	96.4	55.3

6.3.5 TG/DTA

Figure 6.7 (a) presents the mass loss and heat flow curves of M40 samples before and after 6 months of exposure to SC condition. As a similar trend was

obtained under all the conditions utilized in this study, a single graph was used to represent the decomposition behavior of each sample. According to the mass loss shown on the TGA curves, the decomposition steps of M40 samples can be divided into 3 main stages: (i) 40-300 °C due to the loss of unbound water and the dehydration of hydromagnesite, (ii) 300-500 °C due to the decomposition of any uncarbonated brucite and the dehydroxylation of hydromagnesite, and (iii) 500-800 °C due to the decarbonation of hydromagnesite and magnesite (i.e. residual/undecomposed during the production of MgO cement). For M20F20 (Figure 6.7(b)) and M20G20 (Figure 6.7(c)) samples, the decomposition steps were slightly different from those of M40 samples at temperatures below 300 °C. Accordingly, the mass loss at 40-170 °C was attributed to the dehydration of M-S-H/C-S-H; whereas the mass loss at 170-300 °C was due to the dehydration of hydrotalcite and M-S-H/C-S-H (Bellotto 1996; Gallucci, Zhang & Scrivener, 2013; Pérez-Ramírez, Mul, Kapteijn & Moulijn, 2001; Zhang, Vandeperre & Cheeseman, 2014). When compared to the initial 28-day (i.e. before exposure) results, all samples experienced a decrease in mass loss after 6 months of exposure, which indicated a reduction in the amount of hydration and carbonation products.

The presence of considerable overlap in the thermal decomposition of different phases in each stage presented a challenge in performing quantitative analysis on the contents of each phase based on mass loss. However, as seen in Table 6.8, there was a clear decline in the mass loss of M40 samples at each temperature range as well as the total mass loss after being subjected to chemical attack for up to 6 months. The degree of mass loss, which was mainly associated with the decomposition of hydrate and carbonate phases such as hydromagnesite, increased with exposure duration, as more phases decomposed over time. The TGA results were consistent with the XRD and strength results in general, where a decrease in mass loss due to decomposition of key phases

corresponded to a reduction in strength after each durability test. The highest mass loss was observed in samples exposed to SS condition, which was in line with the highest decline in strength observed under this condition (Table 6.2). Alternatively, while mass loss was still revealed under FT exposure, it was more subtle as the main reason for strength reduction in samples subjected to FT was the cracking and scaling of concrete due to expansion. Samples M20F20 and M20G20 revealed a similar trend in terms of mass loss, which increased over exposure duration. This reduction in mass was associated with the decomposition of hydrate phases as well as Mg-carbonates such as hydromagnesite, thereby explaining the decline in strength.

Figure 6.7 Mass loss and heat flow curves of (a) M40, (b) M20F20 and (c) M20G20 samples before and after 6 months of exposure to sodium chloride condition

Table 6.8 Mass loss (%) of selected samples at different stages of decomposition obtained by TGA.

Sample	Duration (months)	Temperature range (°C)					Total
		40-170	170-300	40-300	300-500	500-800	
M40	Initial (28 days)	-	-	9.4	14.2	1.8	25.4
M40-SC		-	-	9.0	13.9	1.2	24.1
M40-SS	1	-	-	7.4	12.6	1.1	21.1
M40-FT		-	-	8.6	13.6	1.2	23.4
M40-SW		-	-	8.4	13.6	1.4	23.4
M40-SC		-	-	6.6	12.9	1.6	21.1
M40-SS	6	-	-	5.1	12.1	1.4	18.6
M40-FT		-	-	6.9	13.5	1.4	21.8
M40-SW		-	-	7.2	13.6	1.5	22.3
M20F20	Initial (28 days)	9.2	4.2	-	20.2	1.7	35.3
M20F20-SC	1	8.7	1.4	-	18.7	3.0	31.8
M20F20-SC	6	7.8	1.2	-	17.6	2.0	28.6
M20G20	Initial (28 days)	11.4	3.3	-	16.6	3.2	34.5
M20G20-SC	1	10.5	2.8	-	15.4	3.0	31.7
M20G20-SC	6	9.4	3.4	-	11.7	3.1	27.6

6.3.6 Microstructure

The SEM images of selected samples before (i.e. after 28 days of initial curing) and after 6 months of exposure to SC conditions are shown in Figure 6.8. A comparison of M40 samples before and after exposure (Figure 6.8 (a) and (b)) have revealed the formation of rosette-like hydromagnesite, as confirmed earlier by XRD analysis. The fibrous structure of this HMC demonstrated interlocking properties, which are known to provide strength in MgO cement formulations (Dung & Unluer, 2017b; Liska & Al-Tabbaa, 2012; Ruan & Unluer, 2017a). Exposure to SC did not lead to a significant change in the microstructure of M40 samples as well as the morphology or the amount of hydromagnesite, which were in line with the phase quantification results presented earlier in Table 6.5 (i.e. only a minor decline in the amount of hydromagnesite was observed after 6 months of exposure to SC). This lack of change was an indication of the

stability of MgO-based concrete mixes under SC conditions. Similar to M40 samples, the change in the microstructures of samples M20F20 (Figure 6.8 (c) and (d)) and M20G20 (Figure 6.8 (e) and (f)) before and after exposure was relatively minimal, in which the formation of hydrate and carbonate phases was observed along with unreacted PFA/GGBS and MgO particles. The dense microstructures of these samples could explain their resistance to chemical attack and hence the smaller strength reduction when compared to other samples.

Figure 6.8 SEM images of (a) M40 at 28 days, (b) M40-SC at 6 months, (c) M20F20 at 28 days, (d) M20F20-SC at 6 months, (e) M20G20 at 28 days and (f) M20G20-SC at 6 months

6.4 Conclusions

This study investigated the durability of MgO cement concrete cubes with addition of PFA) or GGBS in four difference conditions: (i) 10% SC solution,

(ii) 10% SS solution, (iii) FT in 10% SC solution, and (iv) seawater. The exposure duration ranged between 1 to 6 months, during which the mechanical performance and microstructural development of samples were continuously investigated. Results showed that the better chemical attack resistance of MgO cement concrete over PC concrete in all conditions up to 6 months due to the stability of HMCs. The addition of PFA/GGBS improve the durability of MgO cement concrete.

7. COMPARISON OF SCALED-UP MGO BLOCKS WITH LAB-SCALE SAMPLES

This chapter focuses on the strength and microstructure of scaled-up MgO cement concrete blocks containing PFA/GGBS by providing a comparison with lab-scale MgO cement samples. Four block mix designs containing 40% cement and 60% coarse aggregate by weight are prepared under this study. The cement binder is composed of: (i) MgO alone, (ii) MgO:PFA = 1:1, (iii) MgO:GGBS = 1:1 and PC alone. Lab-scale cubic samples have a dimension of 50×50×50mm and scaled-up samples have a dimension of 200×100×60mm. The changes in the performance of the samples are evaluated by compressive strength testing. The properties of the carbonation products are identified by XRD and SEM, and the degree of carbonation is obtained by TG/DTA and XRD. A commercial trial is also included to study the practical aspects of the proposed process in an actual block production facility.

7.1 Introduction

For successful commercialization of such a product development, it is vitally important to understand whether it would be possible to manufacture such products on a large commercial scale. A very limited amount of work has been reported on the production of MgO blocks on a large scale so far (Liska, Al-Tabbaa, Carter & Fifield 2012). In order to find out the properties of the different size samples as well as the effect of SCMs on scaled-up MgO cement concrete, this study investigated the difference between scaled-up MgO concrete blocks and lab-scale MgO concrete cubes in respect of mechanical

performance and microstructure. MgO cement and PC were used as cement binder and PFA/GGBS were added in concrete samples to replace MgO cement. The results of this study enabled the understanding the relationship between lab-scale samples and scale-up blocks based on their mechanical performance and microstructure. The superior performance of scaled-up MgO cement samples proved it is promising for commercialization.

7.2 Mix design

Four block mix designs containing 40% cement and 60% coarse aggregate by weight were prepared under this study. The cement binder was composed of: (i) MgO alone, (ii) MgO:PFA= 1:1, (iii) MgO:GGBS= 1:1 and PC alone. The water to cement ratio of the samples was selected to make four mix designs have identical workability (Table 7.1). Two types of samples were prepared. Lab-scale cubic samples had a dimension of 50×50×50mm and scaled-up samples had a dimension of 200×100×60mm (Figure 7.1). Samples were cast and consolidated using a vibrating table and trowel finished, after which they were kept in air curing environments for 24 hours until de-molding. All the MgO-based samples were subjected to accelerated carbonation at 30±2 °C and 80±5% RH under a CO₂ concentration of 10% for 28 days. PC samples were cured in open air with a 80±5% RH.

Table 7.1 Mix compositions investigated under this study

Mix label	Cement content				Aggregate content	w/c ratio
	MgO (%)	PFA	GGBS	PC (%)	Gravel (%)	
M40	40	0	0	0	60	0.60
M20F20	20	20	0	0		0.45
M20G20	20	0	20	0		0.45
P40	0	0	0	40		0.35

Figure 7.1 Samples prepared in the study: (a) scaled-up block (b) lab-scale cube

7.3 Results and discussion

7.3.1 Compressive strength

After 28 days of CO₂ curing, concrete block samples were removed out from the incubator and compressive strength measured. Figure 7.2 shows the strength development of samples after 28 days of curing. By comparing samples containing MgO binder, samples with 40% MgO always showed the highest strength (38.9 MPa), followed by samples with 20% fly ash (38.1 MPa) while 20% GGBS had relatively lower strength (34.6 MPa) than the former. This can

be explained by the lower MgO content in both M20F20 and M20G20 samples. Since the carbonation products of MgO cement proved to provide high strength, lower MgO content lead to lower HMCs content and thus lower strength. Besides, the hydration process of pozzolanic fly ash and GGBS was slow, so the strength difference between M40 samples and M20F20, M20G20 samples was obvious at the first 7 days of curing. The strength of M20F20 and M20G20 samples was 11.9% and 25.7% lower than that of M40 samples. The strength difference became smaller at later stages since abundant hydration products of M20F20 and M20G20 formed. PC samples had lower strength results compared to samples with MgO, which demonstrated the mechanical advantage of MgO cement under carbonation over PC. Lab-scale cubic samples were observed to have higher strength results than scaled-up samples. The large size of the scaled-up samples made it more difficult to let CO₂ to reach inner part of the samples and less carbonation products formed.

Figure 7.2 Compressive strength of lab-scale samples and scaled-up samples

7.3.2 XRD

Figure 7.3 (a) shows XRD patterns of lab-scale and scaled-up M40 samples after 1 and 28 days of CO₂ curing. In M40 samples, the presence of MgO, brucite, hydromagnesite and MgCO₃ can be found after 28 days of curing. The presence of the MgO peak at 43.5° 2 θ indicated incomplete hydration, whereas the brucite peak at 18.7° and 38° 2 θ was an indication of incomplete carbonation. Hydromagnesite (PDF #025-0513) has its highest intensity peaks at ~15.5°, 30.8°, 35.7° and 8.3° 2 θ , which confirmed the presence of hydromagnesite in the samples. Peaks of other HMCs such as dypingite and nesquehonite either overlapped with the main peaks of hydromagnesite or were too small to be observed in the XRD spectrum. By comparing lab-scale samples (M40) and large-scale samples (M40), the intensity of major hydromagnesite peaks were higher in the former, which explained the higher strength of the cubic samples. The quantification of major phases within M40 samples, obtained via Rietveld analysis, are listed in Table 7.2. Brucite transformed into hydromagnesite from 1 day to 28 days of curing. The hydromagnesite content in lab-scale samples was slightly higher than large-scaled samples, which explained the higher strength results of lab-scale samples.

The XRD pattern of M20F20 in Figure 7.3 (b) indicates the existence of mullite, which is the main phase in fly ash. Besides hydromagnesite, hydration products such as brucite and hydrotalcite can also be found, and hydrotalcite was the main strength resource of the samples. M-S-H is an amorphous phase and the board peaks can hardly be observed in the XRD patterns. Less brucite and hydrotalcite can be found in M20F20 samples which indicates slower hydration rate in M20F20 and thus lower strength results. However, the difference of peak intensity between lab-scale samples and scaled-up samples was not as obvious as M40 samples.

XRD pattern of M20G20 samples after 1 and 28 days of CO₂ curing is presented in Figure 7.3 (c). Like M20G20 samples, hydration products (brucite, hydrotalcite) and carbonation product (hydromagnesite) can be found in M20G20 samples, and amorphous C-S-H cannot be observed in the XRD patterns. It can be found that the intensity of peaks of hydromagnesite, hydrotalcite in 28-day samples were higher than those of 1-day samples. This indicates that the hydration and carbonation products increased with time and this leads to increasing strength. This finding is consistent with conclusions in previous studies that HMCs, hydrotalcite, M-S-H and C-S-H are the main source of strength in MgO, MgO/fly ash and MgO/GGBS concrete.

(a)

(b)

(c)

Figure 7.3 XRD pattern of scaled-up samples after (a) M40 (b) M20F20 (c) M20G20 (M: MgO, B: brucite, HM: hydromagnesite, HT: hydrotalcite, Mu: mullite, K: kaolinite, G: gypsum, C: calcite, P: portlandite, Mc: magnesite)

Table 7.2 Quantification of major phases obtained by XRD-Rietveld analysis

Sample	MgO	Brucite	Hydromagnesite
m40 28d	33.6	31.9	34.5
M40 28d	32.2	37.7	30.1
M40 1d	32.7	52	15.3

7.3.3 TG/DTA

Figure 7.4 (a) presents the TGA curves of the lab-scale and scaled-up M40 samples with 1 and 28 days of curing. According to the weight lost shown on the TGA curves, the decomposition steps of samples can be divided into 3 main stages: (i) 40-300°C due to the loss of unbound water and the water of crystallization of hydromagnesite, due to their dehydration, (ii) 300-500°C due to the decomposition of any uncarbonated brucite and the dehydroxylation of hydromagnesite, and (iii) 500-800°C due to the decarbonation process of hydromagnesite and magnesite. For M20F20 and M20G20 samples, the decomposition steps are a little different from that of M40 samples at temperature below 300°C. According to the heat flow data, mass loss at 40-170°C attributes to the dehydration of M-S-H and C-S-H, and mass loss at 170-300°C attributes to dehydration of hydrotalcite, M-S-H and C-S-H.

Table 7.3 presents the mass loss of scaled-up M40, M20F20 and M20G20 samples at different stages that are previously mentioned. Since there are so much overlap of different phases in each stage, it is difficult to do quantitative analysis based on mass loss of each stage. However, in general it is easy to find that the weight loss of scaled-up M40 samples increased at temperature range of 40-300 and 300-500°C as well as the total mass loss from 1 day to 28 days

of curing. This indicates the growth of carbonation product with time, which is in agreement with the XRD result. In addition, more weight loss can be observed in lab-scale samples compared to scaled-up samples.

Figure 7.4 (b) and (c) shows TGA curve of lab-scale and scaled-up M20F20 and M20G20 samples after 1 and 28 days of curing. Mass loss increased from 1 day curing to 28 days curing which might be related to the increasing amount of C-S-H/ M-S-H with CO₂ curing time. The weight loss of M20F20 samples at 300-500 and 500-800°C was larger than that of M20G20 samples. It can be surmised that more hydration and carbonation products formed in M20F20 samples and this is consistent with the XRD and strength results.

Figure 7.4 TGA curves of scaled-up and lab-scale samples (a) MgO samples (b) M20F20 samples (c) M20G20 samples

Table 7.3 Mass loss and CO₂ sequestration capacity of samples obtained by TGA

Samples/ Mass loss (%)	40-170°C	170-300°C	40-300°C	300-500°C	500-800°C	Total
M40 1d	-	-	7.7	17.3	9.5	34.5
M40 28d	-	-	11.6	25.4	12.2	48.2
m40 28d	-	-	13.9	24.1	12.7	50.7
M20F20 1d	10.9	1.6	-	8.6	1.1	22.2
M20F20 28d	12.4	2.8	-	9.8	1.4	25.4
m20f20 28d	12.8	3.1	-	10.1	1.2	26.1
M20G20 1d	10.1	1.4	-	9.1	1.6	19.6
M20G20 28d	11.9	4.6	-	17.4	1.8	34.7
m20g20 28d	11.6	4.4	-	17.5	1.7	34.2

7.3.4 Microstructure

The SEM images of scaled-up M40 samples after 1 and 28 days of curing are shown in Figure 7.5 (a), (b). Other than MgO and brucite, rosette-like formation of hydromagnesite was observed in the samples. The content and size of hydromagnesite increased with curing duration. The fibrous structures of these hydromagnesite demonstrated interlocking properties, which led to an increase in strength after carbonation.

Mg/Si and Ca/Si ratio is ratio of weight percentage of Mg/Ca and Si element in the samples obtained by EDX. Mg/Si and Ca/Si ratio was used to identify the existence of M-S-H and C-S-H in M20F20 and M20G20 samples. Hydromagnesite can also be found in scaled-up M20F20 samples after 1 and 28 days of curing in Figure 7.5 (c), (d). Amorphous gel-like M-S-H was revealed in the images. The value of the Mg/Si ratio in M20F20 samples was between

0.67-1.4 which is in agreement with the Mg/Si ratio of M-S-H in the previous study. In Figure 7.5 (e), (f), less hydromagnesite was observed in M20G20 compared to M20F20 samples, which explains the lower strength of M20G20 samples. The Mg/Si ratio was above 1.4 in M20G20 samples indicating the absence of M-S-H in MG samples. A further look at the Ca/Si ratio of M20G20 samples was between 0.6 and 1.2 which prove the existence of C-S-H.

Figure 7.5 SEM images of scaled-up samples: (a) M40 1d (b) M40 28d (c) M20F20 1d (d) M20F20 28d (e) M20G20 1d (f) M20G20 28d

7.3.5 Commercial trial of MgO cement concrete blocks

A trial of MgO cement concrete blocks has been undertaken in a commercial lab (Figure 7.6). Scaled-up concrete blocks were cured in sealed conditions under 10% CO₂ concentration, followed by the measurement of the compressive strength.

Figure 7.6 Commercial trial of MgO cement concrete blocks

7.4 Conclusions

This study investigated the difference between scaled-up MgO concrete blocks and lab-scale MgO concrete cubes in terms of the mechanical performance and microstructure. MgO cement and PC were used as cement binder and PFA/GGBS were added in concrete samples to replace MgO cement.

Compressive strength results showed that although strength of scaled-up MgO samples was lower than that of small lab-scale MgO samples, scaled-up MgO samples always showed better performance when compared to PC samples. Samples with PFA/GGBS had lower strengths than MgO samples due to the slow hydration of fly ash and GGBS. Phase identification and quantification by SEM, XRD and TGA indicated hydromagnesite and portlandite was the main strength resource for MgO and PC samples respectively and directly related to the strength growth from 1 day to 28 days of curing. The larger size of scaled-up MgO blocks made it difficult for CO₂ penetration leading to lower carbonation. Hydration products such as hydrotalcite, C-S-H and M-S-H can be found in MgO samples with fly ash and GGBS, which makes the strength difference between scaled-up samples and lab-scale samples subtle. A trial of prototype performance found superior performance of scaled-up MgO cement that is promising for commercialization.

8. CONCLUSIONS AND FUTURE WORK

This chapter summarizes the findings obtained and highlights the significance of each study. The main goal of this research is to (i) enhance the carbonation, mechanical performance and microstructural development of MgO cement concrete containing different additives, (ii) evaluate the stability of the formed phases under various conditions involving high temperatures and aggressive environments, and (iii) provide a comparison between commercial and lab scale blocks in terms of performance and microstructure. In line with these goals, initial studies focus on evaluation of the influence of various concrete mix designs on the carbonation and mechanical performance of MgO cement concrete. A novel pre-conditioning technology is used to improve the strength development of MgO cement. Furthermore, the performance and stability of phases in MgO cement concrete subjected to high temperatures of up to 550 °C and various aggressive environments are investigated. Pulverized fly ash (PFA) and ground granulated blast-furnace slag (GGBS) are introduced as supplementary cementitious materials (SCMs) to investigate their influence on MgO cement concrete. Finally, the difference between MgO-based lab-scale and scaled-up concrete blocks are evaluated in terms of their mechanical performance and microstructural development. This is followed by a section on suggestions relating to future work that can be undertaken to advance research in this field.

8.1 Conclusions

The aim of the work presented in this thesis is to (i) enhance the carbonation, mechanical performance and microstructural development of MgO cement concrete containing different additives, (ii) evaluate the stability of the formed phases under various conditions involving high temperatures and aggressive environments, and (iii) provide a comparison between commercial and lab scale blocks in terms of performance and microstructure. This was performed through investigations of different variables by conventional and novel approaches involving mechanical testing and microstructure analysis. Mechanical performance was evaluated via porosity, density and compressive strength measurements of concrete at different durations. Hydration and carbonation processes of MgO cement was studied by isothermal calorimetry, XRD, TG/DTA, SEM/FESEM, EDX, pH measurement and acid digestion analyses under various conditions. The main conclusions from each study are summarized in the following sections.

8.1.1 Influence of the mix design and curing conditions on the performance and microstructure of MgO cement concrete

8.1.1.1 Influence of mix design (i.e. cement and water content)

This study presented the ability of reactive MgO cement-based concrete formulations to carbonate and established a link between the progress of carbonation along the sample cross-sections and overall mechanical performance. A comparison between MgO and PC samples was provided in terms of carbonation degree, microstructure and strength gain. SEM, XRD, TGA, pH measurement and acid digestion analyses provided information on the

hydration and carbonation phases, amount of CO₂ absorbed, morphology and carbonation progress at different sample depths.

MgO samples achieved strengths as high as 13.5 MPa only after 1 day of curing, which is almost twice the strength requirement for masonry blocks (i.e. 7 MPa). The use of MgO in the prepared formulations led to > 80% higher strengths than corresponding PC samples after 7 days of curing under 10% CO₂. These results indicated the feasibility of using reactive MgO as the main binder in the production of construction blocks. The fast strength development observed during the first 7 days stabilized afterwards, which was attributed to the decrease of CO₂ diffusivity within the reduced pore space that was filled up with hydration and carbonation products.

The progress of carbonation depended on the cement and water contents, which also influenced the strength development. The reaction of MgO with H₂O and CO₂ could be further improved as not all the available MgO was utilized in the hydration and subsequent carbonation reactions. The presence of water slowed down the initial (< 3 days) carbonation due to the slow diffusion of CO₂ within the saturated pore network, whereas the availability of excess water enabled the continuation of carbonation in the longer term (> 3 days). Carbonation initially occurred on the sample surfaces and gradually proceeded towards the inner cores. Carbonation degree decreased with an increase in sample depth and increased with curing duration. MgO samples revealed higher carbonation degrees than corresponding PC samples (45% vs. 22% at 14 days). An abundant formation of HMCs such as hydromagnesite, dypingite and nesquehonite was observed along the cross-section of the MgO samples, resulting in a 7-day strength of 24 MPa.

These results indicate the potential of MgO cement samples to reach high strength in a short duration via the carbonation process. This study achieves a better understanding of the carbonation mechanism of MgO cement and provides ideal mix design and curing condition parameters that can be used in the following studies.

8.1.1.2 Use of pre-conditioning

This study investigated the effects of several factors, such as temperature, humidity and pre-conditioning duration on the mechanical performance and microstructural development of MgO cement in comparison to Portland cement. Hydration degree under different conditions was studied by isothermal calorimetry and TGA on paste samples. Microstructural changes and quantitative analysis of the composition of the samples subjected to different pre-conditioning after 56 days of curing were studied by XRD, TGA and SEM.

Elevated temperatures enhanced the hydration process during pre-conditioning, i.e. the higher the temperature the samples were subjected to, the higher was their strength obtained after 56 days of curing. Pre-conditioning at 50 and 60 °C lead to the most effective improvement of the hydration process. When compared to the control mix, whose hydration degree was limited to 43%, increasing the temperature to 60 °C enhanced the hydration process and increased the hydration degree to 65% at the end of 3 days. The strength of 60-2d and 50-2d samples was 16.4% and 22.8% higher than that of the control sample.

Microstructural analysis revealed hydromagnesite as the main strength providing carbonate phase in all samples. Subjecting the samples to elevated

temperatures in pre-conditioning caused an increase in the amount and improved the morphology of hydromagnesite, which was more pronounced at higher temperatures and longer exposure durations. Along with the content, the size of hydromagnesite crystals increased under higher temperatures, which indicated that pre-conditioning enhanced the hydration and carbonation processes of MgO cement samples.

The findings of this study indicated the significant potential of pre-conditioning in achieving high strengths within MgO cement concrete samples only after a few days of curing. As demonstrated, the rate and degree of hydration and the morphology of the final carbonate phases could be enhanced by increasing the temperature and duration of pre-conditioning, leading to significant improvements in the mechanical performance. This provided an easy and energy-efficient way to enhance the mechanical performance of MgO cement concrete.

8.1.2 Performance and microstructure of carbonated MgO cement concrete under high temperatures

This study investigated the changes in the performance and microstructure of carbonated MgO samples subjected to a range of temperatures under different conditions. The variations in sample performance were attributed to the conditions influencing the stability and transformation of carbonate phases, which are the main source of strength in carbonated MgO formulations. Microstructural analysis included the identification of key phases and their quantification under a wide range of conditions. Links between carbonate content, morphology and sample performance were established at different temperatures ranging between 40 and 550 °C and exposure durations of up to 28 days under water, oven and furnace conditions. A combination of various

microstructural analyses was used to discuss the relationship between the amount and properties of carbonate phases and strength development.

When compared to the control sample, the strengths of samples subjected to elevated temperatures of up to 80 °C in water and oven did not indicate a significant deterioration and remained relatively stable. A noticeable decline in sample strength was observed in those exposed to higher temperatures up to 550 °C in a furnace. The poor performance became more obvious as the temperature and exposure duration increased. These changes were associated with the alteration of sample microstructure at elevated temperatures. Microstructural analysis revealed hydromagnesite as the main strength-providing carbonate phase in all samples. Subjecting the concrete to elevated temperatures caused a reduction in the amount and morphology of hydromagnesite, which was more pronounced at higher temperatures and longer exposure durations. Along with the content, the size of hydromagnesite crystals reduced and finally disappeared under high temperatures, which explained the reduction in strength. Quantitative analysis of major phases within each sample revealed a decrease in hydromagnesite content, which was accompanied by an increase in brucite content under increasing temperatures of up to 350 °C. A further increase in temperature to 550 °C led to a decrease in brucite as well as an increase in MgO content, highlighting the decomposition patterns of hydrate and carbonate phases.

These results have shed a light on the development of MgO-based construction products that gain strength via carbonation. Overall, the findings clearly indicate changes in the performance of carbonated MgO samples under elevated temperatures. The stability of samples until 80 °C was demonstrated. The decarbonation of hydromagnesite into brucite, followed by the decomposition of brucite into MgO at higher temperatures of ≥ 350 °C explained the

deterioration of sample performance, which can be further adjusted depending on end use.

This research studied the performance and stability of carbonated Mg-phases under high temperatures for the first time. The investigations not only facilitate understanding and controlling properties that affect the stability of the strength providing phases, but also form a pathway for the development of a range of MgO-based construction products relying on the sequestration of CO₂ for strength gain.

8.1.3 Durability of carbonated MgO cement concrete containing fly ash and ground granulated blast-furnace slag

Although the strength development and reaction products of carbonated MgO cement mixes with and without PFA and/or GGBS have been reported, there is very limited information on the performance of these samples under various durability conditions such as chloride and sulfate attack, freeze-thaw cycling and seawater exposure. In order to fill this gap in the literature, this study aimed to investigate the performance of MgO-PFA and MgO-GGBS based mixes under different environments, whose influence on strength development was evaluated via a comparison of these mixes to PC-based concrete samples subjected to the same environments. Variations in sample performance were explained by a detailed microstructural analysis that revealed the changes in key phases, which controlled the strength development of MgO-based mixes.

Amongst all the conditions used, SS exposure led to the most obvious reduction (10.7-17.8%) in strength at 6 months, whereas seawater had the smallest influence (5.8-6.9%) on strength results. MgO-based samples showed higher strength results both before and after the durability tests when compared to PC-

based samples. The higher resistance of MgO cement samples in SS and FT environments was associated with the stability of their phases under aggressive environments. The reduction in the performance of MgO cement samples at longer exposure durations was mainly associated with the decomposition of hydrate and carbonate phases such as hydromagnesite. The inclusion of PFA and GGBS led to lower reductions in strength due to their filler effect that led to denser microstructures and the formation of hydrate phases that were stable under the tested conditions. When compared to PC-based mixes, the comparable performance of MgO-based samples under these aggressive environments could shed light on the use of these binders at a larger scale.

8.1.4 Comparison of scaled-up MgO blocks with lab-scale samples

This study presented the mechanical performance and microstructural investigation of scaled-up MgO concrete blocks with the addition of fly ash or GGBS. A comparison between scaled-up concrete blocks and lab-scale blocks was provided in terms of compressive strength. Results obtained via XRD, TGA and SEM/EDX analyses provided the change of chemical composition and microstructure with time in both the lab-scale and scaled-up concrete samples.

For both scaled-up and lab-scale samples, M40 samples always had the highest strength results, followed by M20F20 samples, whereas M20G20 had relatively lower strengths. The lower strengths of M20F20 and M20G20 samples at early ages were related to the relatively slow hydration process of the pozzolanic materials. Lab-scale cubic samples were observed to have higher strengths than scaled-up samples. This difference in performance was associated with the large size of the scaled-up samples, which made it more difficult for CO₂ to diffuse through the inner parts of the samples, resulting in a lower carbonation degree.

Samples including MgO as the main binder showed obvious mechanical advantage over PC-based samples as the strength of P40 samples was 22.5% lower than M40 samples after 28 days of curing.

XRD, TGA and FESEM/EDX results indicated the existence of brucite and hydromagnesite in M40 samples. M-S-H and hydrotalcite were found in the M20F20 samples; whereas C-S-H and hydrotalcite were the main phases observed in the M20G20 samples. Formation of hydration products (M-S-H, C-S-H and hydrotalcite) and carbonation products (hydromagnesite/dypingite) increased with curing duration, which explained the increase in strength. The small difference in the compressive strength of the lab-scale and scaled-up M20F20 and M20G20 samples was associated with the formation of hydration products, which did not depend on the carbonation process. The results showed a similar profile of hydration and carbonation products in the lab-scale and scaled-up samples, both of which indicated a similar development from 1 to 28 days of curing.

A commercial trial was also undertaken to study the practical performance of the prepared formulations in real life. Although there was a slight difference between the lab-scale and scaled-up samples with respect to their compressive strengths, carbonated MgO samples revealed better mechanical performance over PC samples, which indicated that feasibility of using MgO as the main binder in non-structural applications, such as commercial concrete blocks.

8.2 Future work

The aim of this research was to enhance the carbonation and mechanical performance of concrete mixes involving MgO cements, with the goal of

developing sustainable construction products with high strengths. The findings reported in this study could be expanded to further enhance the performance and sustainability of MgO-based concrete in future studies, as detailed below.

8.2.1 Investigation of the mechanical performance and microstructure of MgO cement concrete containing SCMs under high temperatures

PFA and GGBS were used as supplementary cementitious materials to replace part of the main cement binder in some of the studies included in this report. The use of PFA/GGBS was shown to improve the performance of concrete due to their hydraulic or pozzolanic activity and the reduction in porosity due to the filler effect they provided. MgO cement concrete proved to have good mechanical performance under high temperatures in this study, which indicated its potential to be used in various applications. While some studies have reported the advantages of PC-based mixes containing PFA/GGBS when subjected to high temperatures of up to 800 °C (Ibrahim, Hamid & Taha, 2012; Kong, Sanjayan & Sagoe-Crentsil, 2007; Poon, Azhar, Anson & Wong, 2001, 2003; Zhang, Kodur, Qi, Cao & Wu, 2014), further work can be performed on the stability and transformation of phases that form within hydrated and carbonated MgO-PFA/GGBS formulations under high temperatures.

8.2.2 The use of carbonation modelling to study the influence of different parameters on the long-term carbonation and mechanical performance of MgO mixes

Although the influence of several factors on the carbonation of PC and MgO mixes has been studied before, none of these parameters individually determine the extent of carbonation. The optimum combination of these conditions that will achieve complete hydration and carbonation, and associated maximum strength gain, needs to be determined. Optimization of the carbonation

conditions is a complex task since it involves a wide range of aspects and variables. All the previous studies performed on MgO cements so far have been performed on an experimental platform. This is not only time consuming but also provides limited information, especially on the long-term properties of the developed formulations. Alternatively, several studies have reported the carbonation mechanisms of PC mixes via both experimental results and modelling (Hyvert 2010; Kashef-Haghighi, Shao & Ghoshal, 2015; Marques, Chastre & Nunes, 2013; Talukdar, Banthia & Grace, 2012). Some of the main factors studied include mix composition, CO₂ concentration, temperature, humidity and inclusion of supplementary materials. As these models are generally based on assumptions that are applicable for a range of concrete mixes, they can be utilized in studying the carbonation mechanisms of concrete mixes containing MgO cements.

8.2.3 Investigation of the mechanical performance and microstructure of MgO cement concrete containing recycled aggregates

MgO cement concrete is known to have several sustainability advantages over PC including its ability to gain strength by sequestering CO₂, its lower production temperatures, ease of manufacturing, improved mechanical performance and durability and ability to combine with waste materials. In order to increase the sustainability of MgO-based formulations, recycled aggregates can be incorporated in the developed mix designs. Different types and content of recycled aggregates has been used in previous studies, where their influence on the overall mechanical performance and durability of PC-based concrete mixes was studied (Berndt, 2009; Evangelista & De Brito, 2010; Sagoe-Crentsil, Brown & Taylor, 2001; Tabsh & Abdelfatah, 2009). A similar approach can be applied to MgO cement mixes by investigating the feasibility of developing

sustainable MgO-based concrete formulations involving the use of recycled aggregates together with PFA/GGBS.

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