Mechanical performance and microstructural development of MgO-SiO₂-H₂O systems

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2018

Sonat, C. (2018). Mechanical performance and microstructural development of MgO-SiO₂-H₂O systems. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/80896>

<https://doi.org/10.32657/10220/47439>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**MECHANICAL PERFORMANCE AND
MICROSTRUCTURAL DEVELOPMENT OF
MgO-SiO₂-H₂O SYSTEMS**

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School of Civil and Environmental Engineering

2019

**MECHANICAL PERFORMANCE AND
MICROSTRUCTURAL DEVELOPMENT OF
MgO-SiO₂-H₂O SYSTEMS**

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

2019

ACKNOWLEDGEMENTS

This work was undertaken in the Protective Engineering (PE) and Environmental Engineering Laboratories, School of Civil and Environmental Engineering at the Nanyang Technological University.

I would like to express my deep sense of gratitude to my supervisor Dr. Cise Unluer for giving me the opportunity to carry out my Ph.D. in NTU. This research would not have been possible without her valuable inputs, continuous guidance and patience all through the research and writing phase.

I am thankful to all final year project (FYP) students Chin Haow Lim, Pham Viet Hoang, Eng Hui Lim, Wen Wei Teo and Chong Han Lim, for their hard work and contribution to my project.

My sincere thanks goes to the laboratory technicians (Mr. Phua, Mr. Cheng, Mr. Jeffrey, Mr. Chan, Mr. Goh, Mr. Ho, Mr. Subas, Mr. David, Mrs. Lim, Mr. Han Khiang, Mr. Ong, Maria and Pearlyn) in Protective Engineering (PE), Construction Technology (CT) and Environmental Engineering Laboratories for their assistance regarding laboratory techniques, equipment and official paperwork.

I would like to thank to my groupmembers Haoliang Dong, Jiawei Liu, Liyun Pu, Shaoqin Ruan, Dr. Nguyen Tien Dung, Dr. GVP Bhagath Singh and Dr. Sanjeev Kumar. I am also very thankful to my colleagues Li Ye, Yiquan, Jishen, Weiping, Mukund, Dr. Zhitao, Jiawei Lei, Deepesh, Gizem Mestav Sarica and H. Enis Karahan for sharing their experience regarding coursework and laboratory work. A special thanks goes to Alper Aldemir for being so credible even from kilometers away.

Last but not the least, I am very grateful to my family and my friends, who has always encouraged and supported me throughout my studies.

ABSTRACT

Reactive magnesium oxide (MgO)-based cement mixes present several advantages due to their lower production temperatures than Portland cement (PC), similar rate of strength development when compared to PC mixes, and ability to be produced from various alternative routes involving waste materials such as reject brine or seawater. The combination of reactive MgO and SiO₂ leads to formation of magnesium-silicate-hydrate (M-S-H), which is known to contribute to significant strength gain in cement-based formulations. The high performance achieved by MgO-SiO₂ mixes under ambient conditions has led to scientific interest in the exploration of their potential to be utilized in structural and non-structural construction applications. In line with this interest, the main goal of this study was to analyse the mechanical performance and microstructural development of MgO-SiO₂-H₂O systems and evaluate the stability of the formed phases under various conditions.

Initial investigations focused on the effect of mix design as well as different curing conditions on the strength development of MgO-SiO₂ mixes. Furthermore, the use of waste materials such as rice husk ash (RHA), which replaced microsilica as a SiO₂ source in MgO-SiO₂ formulations, was investigated to improve the environmental and economical aspects of the developed mixes. These efforts were followed by the development of a multi-component binder, which involved the formation of a dense network composed of both hydrate and carbonate phases via the introduction of carbonation in the MgO-SiO₂-H₂O system. Finally, the developed formulations were tested under different durability conditions for an assessment of their performance and stability under aggressive environments. These investigations involved the use of isothermal calorimetry and pH measurements to analyse the hydration process. Mechanical performance was assessed via compressive strength measurements at different durations. Microstructural analysis was performed via various techniques such as x-ray diffraction (XRD), thermogravimetric/derivative thermogravimetric analysis (TG/DTG), Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM).

In the initial studies, where the influence of mix design and different curing conditions

were discussed, mix compositions with a MgO/SiO_2 weight ratio of 1-1.5 resulted in the best mechanical performance, depending on the water/binder ratio. Although elevated temperatures (60°C) led to rapid strength development and M-S-H formation at early ages, high humidity sealed curing resulted in the best long-term mechanical performance within $\text{MgO}-\text{SiO}_2-\text{H}_2\text{O}$ systems. From these results, a correlation between the compressive strength and the formed M-S-H content was established. Studies on the use of alternative silica sources such as RHA demonstrated that amorphous RHA can effectively be used as a silica source in $\text{MgO}-\text{SiO}_2$ formulations to partially or fully replace microsilica. Evident formation of M-S-H led to a satisfactory mechanical performance within samples incorporating amorphous RHA. Further studies investigated the incorporation of carbonation curing in $\text{MgO}-\text{SiO}_2$ systems, which enhanced strength development. This increase in strength was associated with the densification of microstructure via the formation of Mg-carbonates, which were assessed via microstructural analysis. Finally, subjecting $\text{MgO}-\text{SiO}_2$ samples under different durability conditions for up to 180 days revealed that $\text{MgO}-\text{SiO}_2$ based concrete maintained its strength development under various aggressive environments and performed better than PC-based concrete samples under magnesium chloride (MgCl_2) and magnesium sulfate (MgSO_4) environments. This advantageous performance of $\text{MgO}-\text{SiO}_2$ samples was associated with the stability of hydrate phases, namely brucite ($\text{Mg}(\text{OH})_2$) and M-S-H, under several durability environments including carbonation, sodium chloride (NaCl), MgCl_2 and MgSO_4 environments.

The findings of this research shed light on the enhancement of the performance of $\text{MgO}-\text{SiO}_2$ based formulations through a detailed investigation of key parameters such as mix design, curing conditions, use of alternative materials and durability. The obtained results contribute to the literature via the information generated on the formation and stability of hydrate phases under various conditions and their effect on the strength and microstructural development of $\text{MgO}-\text{SiO}_2$ mixes. When compared to similar PC-based mixes, the $\text{MgO}-\text{SiO}_2$ formulations developed in this study demonstrated the potential to be used in various building applications due their satisfactory mechanical performance and durability under various environmental conditions.

LIST OF PUBLICATIONS

Publications derived from the work in the thesis are listed below:

- ❖ C. Sonat, N. Dung, C. Unluer, Performance and microstructural development of MgO–SiO₂ binders under different curing conditions, *Construction and Building Materials* 154 (2017) 945-955.
- ❖ C. Sonat, C. Unluer, Investigation of the performance and thermal decomposition of MgO and MgO-SiO₂ formulations, *Thermochimica Acta* 655 (2017) 251-261.
- ❖ C. Sonat, C. Unluer, Investigation of the mechanical properties of MgO-SiO₂ binders, 37th Cement and Concrete Science Conference, London, 2017.
- ❖ C. Sonat, W.W. Teo, C. Unluer, Performance and microstructure of MgO-SiO₂ concrete under different environments, *Construction and Building Materials* 184 (2018) 549-564.
- ❖ C. Sonat, C. Unluer, Development of magnesium-silicate-hydrate (MSH) cement with rice husk ash, *Journal of Cleaner Production* 211 (2019) 787-803.

Other related publications:

- ❖ E.T. Gall, C. Sonat, W. W. Nazaroff and C. Unluer, Investigating CO₂ removal by Ca-and Mg-based sorbents with application to indoor air treatment. *Building and Environment* 110 (2016) 161-172.
- ❖ C. Sonat, C.H. Lim, M. Liska and C. Unluer, Recycling and reuse of reactive MgO cements—A feasibility study. *Construction and Building Materials* 157 (2017) 172-181.

LIST OF ACRONYMS

CH	Calcium hydroxide
CO ₂	Carbon dioxide
CS	Compressive strength
C-S-H	Calcium silicate hydrate
DTG	Derivative thermogravimetry
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
LOI	Loss on ignition
Mg ⁺²	Magnesium ion
MgCl ₂	Magnesium chloride
MgO	Magnesium oxide
Mg(OH) ₂	Magnesium hydroxide – brucite
MgSO ₄	Magnesium sulphate
MgCO ₃	Magnesium carbonate – magnesite
MS	Microsilica
M-S-H	Magnesium silicate hydrate
NaCl	Sodium chloride
PC	Portland cement
pH	Negative logarithm of hydrogen ion concentration
RH	Relative humidity
RHA	Rice husk ash
RHA-a	Amorphous rice husk ash
RHA-c	Crystalline rice husk ash

RIR	Reference intensity ratio
SHMP	Sodium hexametaphosphate
SiO ₂	Silicon dioxide - silica
TG	Thermogravimetry
TGA	Thermogravimetric analysis
w/b	Water to binder ratio
XRD	X-ray diffraction

LIST OF SAMPLE LABELINGS IN BODY CHAPTERS

Chapter 4

S sample	Sample cured under sealed conditions
A sample	Sample cured under ambient conditions
W30 sample	Sample cured under water at 30 °C
W60 sample	Sample cured under water at 60 °C
O sample	Sample cured in oven

Chapter 5

Ra sample	MgO-SiO ₂ based sample consisting of RHA-a as its silica source
Ra-M sample	MgO-SiO ₂ based sample consisting of RHA-a and MS as its silica sources
M sample	MgO-SiO ₂ based sample consisting of MS as its silica source
Rc sample	MgO-SiO ₂ based sample consisting of RHA-c as its silica source

Chapter 6

M samples	Samples consisting of solely MgO as binder
M-S sample	M sample cured under sealed conditions
M-C sample	M sample cured under carbonated conditions
MS samples	Samples consisting of MgO and SiO ₂ as binder
MS-S sample	MS sample cured under sealed conditions
MS-C sample	MS sample cured under carbonated conditions

Chapter 7

M samples	MgO-SiO ₂ based samples
P samples	PC based samples
C sample	Control sample, cured under control (i.e. sealed) conditions
CA sample	Sample cured under carbonated conditions
W sample	Sample cured under water
SC sample	Sample cured under sodium chloride (NaCl) solution
MC sample	Sample cured under magnesium chloride (MgCl ₂) solution
MSu sample	Sample cured under magnesium sulphate (MgSO ₄) solution

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Chapter 1: INTRODUCTION

1.1. Research background

The high energy requirement and carbon dioxide (CO₂) emissions associated with the production of Portland cement (PC), amounting to over 8% of global anthropogenic emissions (WBCSD, 2009), has led to the development of alternative cementitious binding materials with lower environmental impacts. One class of alternative binders is reactive magnesium oxide (MgO) cements, which have received significant attention from the industry and academia in recent years (Pearce, 2002).

MgO can be obtained by the calcination of magnesium carbonate minerals (Shand, 2006; Cise Unluer, 2012; C Unluer & Al-Tabbaa, 2013; C. Unluer & Al-Tabbaa, 2014) and from seawater or brine sources (V. Ferrini, C. De Vito, & S. Mignardi, 2009; Mignardi, De Vito, Ferrini, & Martin, 2011). It can also be derived from magnesium silicates, which has been suggested as a part of a newly developed low-carbon cement system (Flatt, Roussel, & Cheeseman, 2012). MgO is classified as “reactive”, “hard-burned”, “dead-burned” or “fused” depending on the calcination temperature used during its production. Light-burned (i.e. reactive or caustic) MgO is calcined at 700-1000 °C and has a very high specific surface area (SSA) and reactivity. The properties and applications of light-burned MgO have been reported in several studies (V. Birchal, 2001; Caraballo, Roetting, Macias, Miguel Nieto, & Ayora, 2009; Chau & Li, 2008; Fukumoto, Sasaki, Moriyama, & Hirajima, 2011; Garcia et al., 2004; Jensen, Aaes, & Madsen, 1986; Jin & Al-Tabbaa, 2014a; Rotting, Cama, Ayora, Cortina, & De Pablo, 2006; C. Unluer & Al-Tabbaa, 2014), including its use in cementitious materials (M. Liska & A. Al-Tabbaa, 2009; Mo & Panesar, 2012; C. Unluer & Al-Tabbaa, 2011; L. Vandeperre, Liska, & Al-Tabbaa, 2008b; L. J. Vandeperre & Al-Tabbaa, 2007; L. J. Vandeperre, Liska, & Al-Tabbaa, 2007). Hard-burned MgO is calcined at 1000-1400 °C and has a relatively low SSA

and reactivity. It is typically used in applications that exploit the expansion properties of MgO (P. Gao et al., 2008; Mo, Deng, Tang, & Al-Tabbaa, 2014). Dead-burned MgO (periclase) is calcined at 1400-2000 °C, has a low SSA and is unreactive (Wagh, 2004). It is mainly used in refractories (Ghanbari Ahari, Sharp, & Lee, 2002; Silva, Aneziris, & Brito, 2011). Calcined above 2000 °C is “fused MgO”, which possesses low hydration energy, high thermal shock resistance, and a compact structure. It is used in monolithic refractories and electrical insulating (Canterford, 1985; J. Li, Zhang, Shao, & Zhang, 2015).

The main applications of MgO within the construction industry include: (i) magnesium oxychloride (MOC) cements which are used in fiber reinforced fire resistant boards (Sorrel & Armstrong, 1976; Urwongse & Sorrell, 1980), (ii) magnesium oxysulfate (MOS) cements used in lightweight insulation panels (Beaudoin & Feldman, 1977; Beaudoin & Ramachandran, 1978), (iii) magnesium phosphate (MAP) cements used in fire protection and rapid repairs (Mestres & Ginebra, 2011; Ribeiro & Morelli, 2009; Viani & Gualtieri, 2014), and (iv) magnesium expansive additives (MEA) used to compensate concrete shrinkage in dam construction (P.-W. Gao, Xu, Chen, Li, & Lu, 2013; P. Gao et al., 2008; Mo, Deng, & Tang, 2010; Mo et al., 2014; Zheng, Xuehua, & Mingshu, 1991). Recent research on the use of reactive MgO has identified its ability to gain strength by carbonation, which has led to the development of porous applications with the ability to permanently sequester CO₂ during curing (M. Liska & A. Al-Tabbaa, 2009; L. Vandeperre et al., 2008b; Yi, Liska, & Al-Tabbaa, 2012).

Main advantages of MgO cements include their: (i) ability to sequester CO₂ and gain strength by the formation of hydrated magnesium carbonates (HMCs), (ii) high fire resistance, (iii) high durability performance in extreme and aggressive environments, (iv) lower sensitivity to impurities enabling the use of industrial by-products and (v) potential to be fully recycled when MgO is used alone as a binder (Sonat, Lim, Liska, & Unluer, 2017). Major issues include unfamiliarity and insufficient track record compared to the high validation and market confidence in PC, which can be overcome with a well-planned research agenda generating long-term results.

In addition to systems consisting solely of reactive MgO as the main binder (Dung & Unluer, 2016), blended systems of reactive MgO with Portland cement (PC) (M Liska & Al-Tabbaa, 2008), ground granulated blastfurnace slag (Jin, Gu, Abdollahzadeh, & Al-Tabbaa, 2015) and fly ash (L. Vandeperre, Liska, & Al-Tabbaa, 2008a) have been studied previously. Differing from carbonated formulations in terms of reaction mechanisms, the use of reactive MgO in MgO-SiO₂-H₂O systems leads to the formation of magnesium silicate hydrate (M-S-H). Previous studies reported M-S-H gel as a non-cementitious material (Cohen & Bentur, 1988b), whereas recent works have shown the formation of M-S-H to demonstrate cementitious properties (Jin & Al-Tabbaa, 2013, 2014b; Tingting Zhang, Luc J. Vandeperre, & Christopher R. Cheeseman, 2014a), which can be useful in different applications ranging from waste encapsulation (T. Zhang, C. R. Cheeseman, & L. J. Vandeperre, 2011b) to refractory castables (Sako, Braulio, & Pandolfelli, 2012; J. Szczerba, Prorok, Snizek, Madej, & Maslona, 2013). M-S-H, whose cementitious properties have been reported earlier, can be obtained by chemical synthesis (e.g. reaction of sodium metasilicate (Na₂SiO₃·5H₂O) and magnesium nitrate (Mg(NO₃)₂·6H₂O)) (D. R. M. Brew & F. P. Glasser, 2005) or via the reaction between reactive magnesium oxide (MgO) and a silica source such as microsilica. (Jin & Al-Tabbaa, 2013, 2014b; Z. Li et al., 2014b; J. Szczerba et al., 2013; Takahashi, Tanaka, Satoh, & Endo, 1994; Jiangxiong Wei, Yu, Zhang, & Zhang, 2011a; T. Zhang et al., 2011b; T. Zhang et al., 2014a). The reduction of water content through the use of sodium hexametphosphate (SHMP) in MgO-silica fume mixes was reported to enable 28-day strengths as high as 70 MPa (Tingting Zhang, Luc J Vandeperre, & Christopher R Cheeseman, 2014b).

The research presented in this thesis focuses on the mechanical performance and microstructural development of MgO-SiO₂-H₂O systems. The hydration of MgO-SiO₂ formulations, leading to the formation of M-S-H gel, was studied in detail. The presented work involved the investigation of several variables including the influence

of mix design and curing conditions, use of alternative silica sources, carbonation curing and performance of MgO-SiO₂ concrete under aggressive environments. The findings of this research contributed to the existing literature on MgO-SiO₂ based formulations via the understanding developed on the hydration mechanisms, influence of various conditions and the enhanced strength development provided within the developed formulations.

1.2. Aims, objectives and novelty of the research

The primary aim of this research is to investigate the mechanical performance and microstructural development of MgO-SiO₂ formulations through the investigation of different variables. The objectives of this research topic were:

1. Optimization of the mix design (MgO/SiO₂ ratio, water/binder ratio, sodium hexametaphosphate (SHMP) content) to obtain the highest mechanical performance coupled with an effective dispersion of MgO and microsilica;
2. Investigation of the influence of curing conditions, including elevated temperatures, under water curing, different humidity levels, on the performance and microstructure of MgO-SiO₂ formulations;
3. Utilization of waste material (i.e. rice husk ash) as a silica source to produce M-S-H and examination of the final products in terms of mechanical performance and microstructure evolution;
4. Development of high strength concrete mixes with the incorporation of carbonation curing in MgO-SiO₂ formulations and identification of the final hydration and carbonation products;
5. Evaluation of the performance of MgO-SiO₂ based binders under aggressive environments and a comparison of their performance with PC-based concrete subjected to the same conditions.

This research involves the formation of M-S-H as a result of the reaction between MgO and a silica source. The formed hydration product can produce high strength

values and act as a cementitious material, especially at reduced water contents. The performance of the final mixes is reported in terms of their workability, stability and strength development under different conditions and durations of curing. The phase formations at the end of selected curing periods are characterized by x-ray diffraction (XRD), thermogravimetric/derivative thermogravimetric analysis (TG/DTG), field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FTIR). This study presents a novel research area as only a very limited number of studies have been reported on the formation, properties, and stability of MgO-SiO₂ formulations, especially within the building materials context. Therefore, the analysis of microstructure and strength development as a function of several parameters such as mix design, curing parameters, use of alternative SiO₂ sources, and aggressive environments is an innovative step in determining the capabilities of MgO-SiO₂ based binders in building applications.

1.3. Layout of the thesis

This thesis consists of 8 chapters in total, the details of which are provided below:

Chapter 1 introduces the research and provides background information about the topics investigated under this research and presents the main goals and objectives.

Chapter 2 provides a detailed relevant literature review focusing on the production and properties of MgO, formation and properties of M-S-H, and carbonation of Mg-based systems. A section about durability of Mg-based binders, in addition to durability of PC concrete, is also included.

Chapter 3 presents the materials used, sample preparation and methodology in all the experiments in this research work.

Chapter 4 focuses on the influence of mix design parameters and curing conditions on the performance of MgO-SiO₂ formulations. The effect of MgO:SiO₂ ratio, water/binder ratio, and superplasticizer content on performance are discussed along with the performance and microstructural development under several curing conditions.

Chapter 5 is dedicated on the use of rice husk ash (RHA), which is a waste material, as a silica source in MgO-SiO₂ formulations to produce M-S-H. The performance and evolution of hydration products are examined via several techniques.

Chapter 6 concentrates on the effect of high humidity sealed curing and carbonation curing on both MgO and MgO-SiO₂ based concrete. The hydration and carbonation products are assessed via several techniques.

Chapter 7 discusses the performance of MgO-SiO₂ based concrete under aggressive conditions by examining both mechanical performance and microstructure of the samples under several environments. The mechanical performance of MgO-SiO₂ based concrete was compared with the PC concrete under exact same conditions.

Chapter 8 highlights the main findings reached and presents guideline for further related studies.

Chapter 2: LITERATURE REVIEW

2.1. Production and properties of MgO

2.1.1. Production of MgO

Magnesium is found in minerals such as dolomite ($\text{CaMg}(\text{CO}_3)_2$) and magnesite (MgCO_3) and is the third most abundant element in seawater (Shand, 2006). MgO is obtained by two major methods: calcination of magnesia-based minerals (e.g. magnesite, dolomite or brucite), and synthetically from brine or seawater.

Calcination of MgCO_3 to form MgO occurs at temperatures between 550-800 °C and is an endothermic reaction, as indicated in Equation 2.1. The lower calcination temperature in the production of reactive MgO cements compared to PC (<800 °C vs. 1450 °C) allows the use of alternative fuels with relatively low heating values.

During calcination of MgCO_3 sintering occurs, reducing the porosity of the product formed. Calcination conditions such as temperature and residence time are key parameters that influence the specific surface area (SSA) and reactivity of the MgO produced (Shand, 2006; Thomas, Musso, Prestini, & Troczynski, 2014). Increasing the calcination temperature and residence time decreases MgO reactivity. This is accompanied by a reduction in the SSA and an increase in particle size (Eubank, 1951; Mo et al., 2010).

MgO can be also obtained from seawater by adding lime (CaO), which causes $\text{Mg}(\text{OH})_2$ to precipitate. This is then heated to produce MgO as shown in Equations 2.2 and 2.3. The product generally contains MgO in a range of 55–98%. The common impurities in MgO include CaO , SiO_2 , Fe_2O_3 , and Al_2O_3 , with concentrations depending on the starting material.

It is estimated that about 14 million tonnes/year of MgO is produced world-wide. For comparison, production of PC exceeds 4 billion tonnes/year (USGS, 2014). The 3.7 billion tonnes of magnesite reserves in China account for ~29% of the world's total reserves (J. Li et al., 2015). Although magnesite resources are widely available, 75% of the global magnesite production is from China, North Korea, Slovakia, Turkey, Russia, Australia and India (Shand, 2006), as shown in Figure 2.1. 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 (Y. Zhang, Li, Xu, Sang, & Jin, 2017). 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 cost of reactive MgO was reported as ~€300/tonne, which was higher than PC (~€70/tonne) (Martin Liska, Al-Tabbaa, Carter, & Fifield, 2012b; Martin Liska, Al-Tabbaa, Fifield, & Carter, 2012).

Figure 2.1 Global distribution of magnesite reserves (Mt = million tonnes, Bt = billion tonnes)

MgO can be present in PC from magnesium carbonate in the raw materials used to produce PC clinker. The production of PC at 1450 °C results in dead-burned MgO, which hydrates slowly under ambient conditions, forming $\text{Mg}(\text{OH})_2$. This is associated with a volume expansion of ~118%, which may be retarded when MgO grains are encapsulated in the concrete matrix. $\text{Mg}(\text{OH})_2$ formation after concrete has hardened can cause structural damage due to delayed expansion. In the 19th century, bridges and viaducts in France and a town hall in Germany constructed using PC containing 16-30% MgO from the dolomitic limestone used in the production of PC suffered from delayed hydration due to expansion of periclase (P.K. Mehta, 1978). This led to limitations on the MgO content in PC to 5% in the UK ("BS EN 197-1: 2000, Cement-part 1: composition, specifications and conformity criteria for common cements," 2007) and China ("GB 175-2007/XG 1-2009, National standard of common portland cements (in Chinese)," 2009) and 6% in the USA to prevent unsoundness at late ages due to delayed expansion of periclase.

2.1.2. Properties of MgO

Factors Influencing Properties of MgO	Properties of MgO	Performance of MgO
<ul style="list-style-type: none">• Properties of parent rock<ol style="list-style-type: none">1. Composition2. Impurities• Calcination conditions<ol style="list-style-type: none">1. Temperature2. Residence time3. Heating rate	<ul style="list-style-type: none">• Reactivity• Specific surface area• Particle size• Agglomeration ratio• pH• Crystal structure• Morphology	<ul style="list-style-type: none">• Expansion• Hydration• Setting time• Carbonation• Others

Figure 2.2 Factors influencing the properties and performance of MgO

MgO exhibits different properties depending on the source and calcination conditions. The main factors influencing the properties and performance of MgO are reactivity, SSA, particle size, agglomeration ratio, crystal structure, pH and morphology (Chau & Li, 2008; Escalante-Garcia, Fuentes, Gorokhovskiy, Fraire-Luna, & Mendoza-Suarez, 2003; Jin & Al-Tabbaa, 2014a; X. Li, 2013; M. Liska, Vandeperre, & Al-Tabbaa, 2006), as shown in Figure 2.2. The SSA determines the reactivity, which also depends on the characteristics of the MgO source and the system in which the MgO is used. The properties of MgO produced from calcination of magnesite or silicates are primarily determined by the calcination conditions and properties of the precursor. For MgO obtained from brine or seawater, preparation methods and precursor properties determine the final properties. These factors influence the hydration and carbonation kinetics of MgO and interactions with other mix components. The processing conditions and properties of raw materials influence the performance of MgO and define: (i) the factors that determine

performance, (ii) potential benefits and limitations of different types of MgO, (iii) performance of MgO with different properties, and (iv) how desirable properties can be produced by customizing specific production parameters according to the intended end use.

The effect of calcination conditions on the production of MgO from magnesium carbonate and magnesium hydroxide using various times and temperatures between 300 and 2000°C has been reported (Aramendia, Borau, & Jiménez, 1996; VS Birchal, Rocha, & Ciminelli, 2000; Eubank, 1951; Liu, Thomas, Ray, & Guerbois, 2007; Mo et al., 2010). SSA, crystal grain size and pore structure, which determine the hydration and expansion behavior, are dependent on calcination conditions. At low temperatures, evaporation of gases causes high porosity, surface area and reactivity. Sintering occurs at higher temperatures (above 900°C) and longer residence times, resulting in increased grain size and lower SSA and pore size. Aramendia et al. (Aramendia et al., 1996) used two different precursors, $\text{Mg}(\text{OH})_2$ and $\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4$, to synthesize MgO and characterized the product formed in air and vacuum. The results showed that MgO with higher SSA and basicity was prepared from $\text{Mg}(\text{OH})_2$ compared to $\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4$. Calcination in a vacuum led to higher SSA and basicity due to the lower activation energy, corresponding to weaker bonds between particles. Alvarado et al. (E. Alvarado, L.M. Torres-Martinez, A.F. Fuentes, & P. Quintana, 2000b) also investigated the effect of the precursors on crystallite size, density, SSA, degree of agglomeration (i.e. the ratio of the primary particle size to the crystallite size) and total porosity. Samples were obtained from magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), magnesium nitrate ($\text{MgNO}_3 \cdot 6\text{H}_2\text{O}$), magnesium acetate ($\text{Mg}(\text{CH}_3\text{CO}_2) \cdot 4\text{H}_2\text{O}$) and dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$). The ideal physical properties (agglomeration ratio of ~1) were obtained using nitrate and acetate salts. The SSA of MgO decreased in the order sulphate > nitrate > acetate > dolomite.

Birchal et al. (VS Birchal et al., 2000) studied the SSA, reactivity and the hydration behavior of six MgO samples calcined at temperatures ranging between 850 and 1000°C, using residence times between 90 to 240 minutes, and reported a correlation between the reactivity and hydration behavior of samples at three temperatures (35, 50, and 90°C). The calcination temperature had a greater

influence on SSA than residence time. Reduction in SSA was observed at calcination temperatures above 900°C. The highest reactivity led to the highest hydration degree of ~70%, which stabilized at ~20% for less reactive samples. In another study (Aramendía et al., 2003), MgO was prepared by: (i) calcination of commercial magnesium hydroxide and carbonate, (ii) calcination of magnesium hydroxide obtained from magnesium nitrate and sulphate, (iii) a sol-gel technique, and (iv) decomposition of urea. The structural and surface properties of the resulting MgO samples were assessed prior to use as catalysts in the Meerwein-Ponndorf-Verley reaction. The most active catalyst was produced by the rehydration and subsequent calcination of MgO obtained from commercial magnesium hydroxide, followed by the MgO from the sulphate precursor. MgO derived from magnesium nitrate and sulphate salts had the highest SSA of 123.7 and 162.5 m²/g, respectively.

Liu et al. (Liu et al., 2007) calcined natural and commercial magnesite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) at temperatures between 500 and 1000°C. As the calcination temperature increased, the SSA and the reactivity of the MgO formed gradually decreased, whereas the crystallite size increased. Basic MgO specimens had higher degrees of hydration than natural MgO (~90% vs. 70% at 24 days). This was attributed to the lower SSA and MgO content (98.5% vs. 80.2%) and larger crystallite size of the latter. Aphane et al. (Aphane, van der Merwe, & Strydom, 2009) studied the time needed for the hydration of MgO produced at three different temperatures (650, 1000, and 1200°C) in magnesium acetate solution and water. The degree of hydration was greater in magnesium acetate solutions than in water due to the extra Mg^{2+} ions. Although the initial rate of hydration was determined by the calcination temperature, all samples eventually achieved the same degree of hydration.

Characterization of reactive MgO obtained from fourteen different sources including magnesite, seawater, and chemical precipitation led to the definition of three categories for MgO reactivity, determined according to the acid reactivity, SSA and agglomeration ratio (Jin & Al-Tabbaa, 2014a). Differences between the calcined and

synthesized MgO samples included: (i) chemical composition: synthetic MgO had a higher Mg content and less impurities than calcined samples; (ii) SSA: higher for synthetic MgO, resulting in a higher reactivity than calcined samples; (iii) agglomeration ratio: ~1 for synthetic MgO (i.e. primary particles were composed of single crystals) and between 1.4 and 7.2 for calcined MgO (i.e. larger primary particles composed of more than one crystallite); and (iv) pH: Lower for synthetic MgO, typically in the range between ~10.10 and 10.75, whereas the pH of calcined samples was between ~10.75 and 12.20 at 90 days due to lower CaO content of the former. A linear relationship between agglomeration ratio and reactivity was observed. An increase in reactivity and hydration rate was found with increasing SSA, until a limit was reached for the degree of hydration at ~80% due to incomplete hydration inside MgO particles.

Calcining magnesite under varying conditions results in MgO samples with different SSA and reactivity, which influence hydration rates. Higher calcination temperatures and longer residence times decrease the inner pore volume, SSA, and therefore the hydration activity of MgO. The type of the precursor and the kinetics of the hydration reaction directly influence the quality and the properties of the end product (Fillipou, Katiforis, Papassiopi, & Adam, 1999; O. Fruhwirth, G.W. Herzog, I. Hollerer, & A. Rachetti, 1985b; Smithson & Bakhshi, 1969). The hydration mechanism of MgO, shown in Equation 2.4, 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 (S.D.F. Rocha, M.B. Mansur, & V.S.T. 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 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 (Fruhirth et al., 1985b).

2.2. Magnesium-silicate-hydrate (M-S-H)

M-S-H was first discovered in 1953 as a minor component in deteriorated sections of a sea-wall concrete. The composition was a combination of 68% M-S-H (i.e. $4\text{MgO}\cdot\text{SiO}_2\cdot 8.5\text{H}_2\text{O}$), 22% CaCO_3 , 9% $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, and 1% free SiO_2 (Bonen, 1992; Cole, 1953). Other forms within the $\text{MgO}\text{-SiO}_2\text{-H}_2\text{O}$ system found in nature include sepiolite ($8\text{MgO}\cdot 12\text{SiO}_2\cdot 6\text{H}_2\text{O}$), talc ($3\text{MgO}\cdot 4\text{SiO}_2\cdot \text{H}_2\text{O}$), serpentine ($3\text{MgO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$), and anthophyllite ($7\text{MgO}\cdot 8\text{SiO}_2\cdot \text{H}_2\text{O}$) (Bowen & Tuttle, 1949).

In $\text{MgO}\text{-SiO}_2\text{-H}_2\text{O}$ systems, Mg^{2+} ions from the dissolution of MgO and formation of $\text{Mg}(\text{OH})_2$ react with hydrated silica to form M-S-H gels. The presence of M-S-H, referred to as a non-cementitious material, is reported as one of the reasons for the deterioration of concrete from sulfate attack, which causes an expansive disruption, leads to the rupture of cementitious matrix, and deteriorates cement paste (Biczók & Szilvássy, 1964; Cohen & Bentur, 1988a; Gollop & Taylor, 1992; Hime & Mather, 1999). M-S-H gels were generally claimed to reduce strength based on the fact that they form during the later stages of sulfate attack (Bonen, 1992). Other investigations of PC pastes suffering from magnesium sulfate attack showed M-S-H forming as a minor constituent (Bonen, 1992; David Bonen & Menashi D Cohen, 1992). Recent studies regarding M-S-H have highlighted its cementitious properties

that lead to high strength development (70 MPa in 28 days), excellent rheological properties, and good alternative for waste encapsulation (Jiangxiong, Yimin, & Yongxin, 2006; Tran & Scott, 2017; T. Zhang, C. Cheeseman, & L. Vandeperre, 2011a; T. Zhang et al., 2014a).

2.2.1. Formation of M-S-H

M-S-H, whose cementitious properties have been reported earlier, can be obtained by chemical synthesis (e.g. reaction of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) and magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)) (D. R. M. Brew & F. P. Glasser, 2005) or via the reaction between Mg-based source (e.g. MgO , $\text{Mg}(\text{OH})_2$) and a silica source such as microsilica (Jin & Al-Tabbaa, 2013, 2014b; Z. Li et al., 2014b; J. Szczerba et al., 2013; Takahashi et al., 1994; Jiangxiong Wei et al., 2011a; T. Zhang et al., 2011b; T. Zhang et al., 2014a).

2.2.1.1. Chemical synthesis of M-S-H

The synthesis of M-S-H has been studied for decades (Bowen & Tuttle, 1949; Yang, 1960). Although the MgO content in PC clinker is usually limited to as low as 1-6% to avoid the unsoundness of cement due to periclase ("BS EN 197-1: 2000, Cement-part 1: composition, specifications and conformity criteria for common cements," 2007; "GB 175-2007/XG 1-2009, National standard of common portland cements (in Chinese)," 2009; RANI, XIANG, ALFONSO, & NIKOLAOS, 2012), MgO can still react with water to form $\text{Mg}(\text{OH})_2$ and M-S-H with a Mg/Si ratio ranging between 4:1 and 1:1 (Bonen, 1992; David Bonen & Menashi D Cohen, 1992). Gollop and Taylor (Gollop & Taylor, 1992) defined M-S-H as a poorly crystallized serpentine with a structure ranging between a true gel and a crystalline phase. Brew and Glasser (D. R. M. Brew & F. P. Glasser, 2005) precipitated M-S-H gel via the: (i) preparation of stock solutions of sodium metasilicate (i.e. $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) and magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), (ii) cooling each solution to about 0°C , (iii) mixing the solutions through the slow addition of the magnesium solution to sodium silicate solution, (iv) settling the precipitate at temperatures of $20\text{-}25^\circ\text{C}$, (v) filtering the precipitate, and (vi) removal of the residual sodium through repeated washing. At the

end of the precipitation process, the composition of Na and unreacted Mg and Si was determined by flame emission and atomic absorption spectroscopy, and UV/visible spectrophotometry. Double decomposition, which involves mixing soluble sodium silicate and magnesium nitrate in certain stoichiometric proportions under a CO₂ insulated environment to prevent the carbonation of the precipitate, can also be used to prepare M-S-H phases (D. M. R. Brew & F. P. Glasser, 2005). Another technique that leads to the precipitation of highly dispersed magnesium silicate was suggested by Krysztafkiewicz et al. (Krysztafkiewicz, Lipska, Ciesielczyk, & Jesionowski, 2004). This method involves mixing solutions of sodium metasilicate and magnesium salts. For the precipitation of products with desirable physicochemical properties, 5-15% NaOH solution was added to the mix. This increased the MgO content within magnesium silicate and enabled the production of a highly dispersed M-S-H gel.

2.2.1.2. M-S-H formation via the reaction between Mg and Si sources

In MgO-SiO₂-H₂O systems, the hydration of MgO to release Mg²⁺ is accompanied by its reaction with the dissolved amorphous silica to form M-S-H, which is responsible for the setting and strength gain of the hydrated matrix (Jin & Al-Tabbaa, 2014b; T. Zhang et al., 2014a). The formation and properties of M-S-H have been studied by several researchers (Jin & Al-Tabbaa, 2013, 2014b; Z. Li et al., 2014b; J. Szczerba et al., 2013; T. Zhang et al., 2011b), followed by recent studies that demonstrated the effect of superplasticizers (i.e. sodium hexametaphosphate) on the formation of M-S-H within MgO-SiO₂ cement pastes (Jia et al., 2016).

The hydration mechanism of MgO is based on the dissolution and precipitation processes (Amaral, Oliveira, Salomão, Frollini, & Pandolfelli, 2010). At the dissolution stage, the released OH⁻ ions are absorbed on the surface of silica particles, increasing the coordination number of the silicon atom, which in turn weakens the oxygen bonds of the underlying silicon atoms. Silica is dissolved and released into the solution as silicate ions, as shown in Equation 2.5 (Jin & Al-

Tabbaa, 2013). At a pH of > 9, the hydrated surface is ionized to form silicon tetrahedral networks ($\text{SiO}(\text{OH})^{3-}$ or $\text{SiO}(\text{OH})^{2-}$), which can be readily complex with metallic cations in solution (Jin & Al-Tabbaa, 2013). Thus, the initial pH of MgO-SiO₂ systems plays a significant role in the formation of M-S-H. The increase in the pH due to the dissolution of MgO enables the dissolution of SiO₂. This is followed by the reaction of Mg²⁺ with aqueous silicon complexes to form M-S-H. The formation of M-S-H is associated with a decrease in the pH value due to the consumption of Mg²⁺. Mg(OH)₂ (brucite) that precipitates during the hydration of MgO can act as a nucleation center during this process, leading to the formation of M-S-H through the deposition of silicon-oxygen layers on magnesium-oxygen octahedral layers (Golubeva, Korytkova, & Gusarov, 2005).

2.2.2. Factors affecting M-S-H formation

The synthesis of M-S-H depends on the ratio and characteristics of the reagents, pH and curing conditions. The reaction degree is related to the availability of dissolved Mg and Si in the solution, which is controlled by the reactivity of MgO and silica, and the pH (Jin & Al-Tabbaa, 2013). Crystalline silica is not as reactive as silicic acid and diatomaceous earth (amorphous biogenic silica), whereas the reactivity of the MgO source decreases in the following order under mild conditions (100-300°C): Magnesium basic carbonate > MgO ≥ MgCO₃ > Mg(OH)₂ (Yang, 1960). Early studies showed that MgO and SiO₂ can react at high temperatures (e.g. 1000°C) (Wunder B, 1997; Yuan, 1990). In 1970s, Kalousek (G.L. Kalousek & C. Lv (translator), 1985; Kalousek & Mui, 1954) demonstrated the reaction between MgO and SiO₂ at 75-350°C. Szczërba et al. (Jacek Szczërba, Prorok, Śnieżek, Madej, & Maślona, 2013) concluded that the first product of the reaction between MgO and H₂O is brucite, which is then converted into an M-S-H phase, forming magnesium silicates (i.e. forsterite and enstatite) at temperatures higher than 500°C. According to Li et al. (Z. Li et al., 2014b), M-S-H gels are more stable than Mg(OH)₂ as the large amounts of

Mg(OH)₂ initially observed during the first few days are greatly reduced after 7 days. The formation of M-S-H gels continues until all the silica fume or Mg(OH)₂ involved in the reaction are fully consumed. Other studies showed that Mg(OH)₂ can react with SiO₂ to form M-S-H under conditions that simulate the earth's mantle conditions at very high pressures and temperatures (D. R. M. Brew & F. P. Glasser, 2005; Bromiley & Pawley, 2003; Yuan, 1990).

The Mg/Si ratio of the reactants also plays an important role in the final composition of M-S-H. The Mg/Si ratio used for the synthesis of M-S-H in a hydrothermal and highly alkaline environment ranges between 0.75 and 1.5, resembling talc and serpentine, respectively (Golubeva et al., 2005; Kalousek & Mui, 1954). Brew and Glasser (D. R. M. Brew & F. P. Glasser, 2005) studied the change in the initial Mg/Si ratios on the formation of M-S-H. The composition of the gels ranged between an Mg/Si ratio of 0.66 and 0.96, while the initial Mg/Si ratio was between 0.67 and 1.5. It was suggested that M-S-H gels do not extend to Mg/Si ratios exceeding 1 as stability is compromised beyond this narrow range (0.66-0.96).

The formation of M-S-H gels is also influenced by the pH of the pore solution within the MgO-silica fume pastes. The variations in pH and Mg²⁺ concentration are determined by the solubility product constant of Mg(OH)₂. Zhang et al. (T. Zhang et al., 2011a) studied the development of M-S-H by changing the pH and showed that in the first 7 days, Mg(OH)₂ was the main reaction product at a pH of 11.3. As the pH value decreased, M-S-H gel started forming, supported by the high concentration of Mg²⁺ and the desirable pH value of the pore solution (~10.5).

In addition to the mix design, properties of precursors and pH of the solution, the formation and properties of M-S-H within MgO-SiO₂ mixes highly depend on the curing conditions (i.e. temperature, humidity and presence of water) (Jiangxiong Wei et al., 2011a). Wei et al. (Jiangxiong Wei, Yu, Zhang, & Zhang, 2011b) concluded

that MgO reacts with silica fume to form $\text{Mg}(\text{OH})_2$ and M-S-H under different temperatures (25°C, 50°C and 100°C with steam curing). The Mg content of M-S-H gel increases with temperature (Mg/Si ratios were 1.32, 1.38, and 1.8 for 25°C, 50°C and 100°C, respectively). Increasing the curing temperature can accelerate the formation of M-S-H gel by increasing the hydration of MgO and dissolution of SiO_2 (J. Szczerba et al., 2013). The exposure of MgO- SiO_2 systems to water was mentioned by (Jin & Al-Tabbaa, 2014b), who noted a decrease in the compressive strength of MgO-microsilica samples after 56 days of underwater curing. This was attributed to the potential dissolving of the M-S-H gel due to the leaching of ions in water.

As the formation of M-S-H is dependent on the hydration of MgO and the availability of Mg^{2+} and OH^- to react with silica, the extent of hydration influences the degree and rate of M-S-H formation and therefore the mechanical performance of the final mix. However, the hydration of even reactive grades of MgO is limited to ~40-80% (Jin & Al-Tabbaa, 2013; Sônia D. F. Rocha, Marcelo B. Mansur, & Virgínia S. T. Ciminelli, 2004). This is attributed to the slow dissolution of MgO and the precipitation of the newly formed $\text{Mg}(\text{OH})_2$ on the surface of MgO particles, which prevents the unhydrated MgO from contacting with water. The limited hydration of MgO can slow down the formation of M-S-H (O. Fruhwirth, G. W. Herzog, I. Hollerer, & A. Rachetti, 1985a; Vermilyea, 1969). This can be overcome with the adjustment of curing conditions to enhance the diffusion of water into the pore solution and thereby promote the dissolution and hydration of MgO.

Slightly elevated temperatures used during the curing process can also increase the dissolution of MgO and SiO_2 , which can improve the formation of M-S-H and therefore the mechanical performance of the resulting formulations. The limited number of studies on the effect of temperature on M-S-H formation have identified that the final composition (i.e. Mg/Si ratio) of M-S-H is influenced by temperature (Jiangxiong Wei et al., 2011a). However, the progress of M-S-H formation under various curing conditions involving different parameters and the impact of these conditions on performance and microstructural development have not been assessed until now.

2.2.3. Properties of M-S-H

The raw materials and preparation method influence the properties of M-S-H. Precipitation of sediments, following the reaction of dissolved sodium metasilicate with selected salts, is one of the main steps in the production of highly dispersed silicate (Krysztalkiewicz, 1988; Werner, Krysztalkiewicz, & Jesionowski, 2000). Many studies performing M-S-H precipitation focus on the optimization of the physicochemical properties of the final product, such as bulk density, capacity to absorb water, particle size distribution, morphology, and microstructure. Magnesium silicate with a large SSA, low bulk density (e.g. 163 g/dm^3), low tendency to absorb water (e.g. $250 \text{ cm}^3/100 \text{ g}$) and dibutyl phthalate (e.g. $350 \text{ cm}^3/100 \text{ g}$), and high capacity to absorb paraffin oil (e.g. $500 \text{ cm}^3/100 \text{ g}$) can easily absorb organic particles (Krysztalkiewicz et al., 2004). The addition of a precipitating agent (sodium metasilicate solution) to a solution of a magnesium salt can facilitate the formation of a highly dispersed product in the precipitation process. The homogeneity can also be improved through the use of a correcting substance such as 5-15% NaOH solution, resulting in a narrow particle size distribution. As the amount of correcting substance increases, the reactivity at the surface of magnesium silicate particles increases, which improves the physicochemical properties of the final product (Krysztalkiewicz et al., 2004; Suda, Tashiro, & Umegaki, 1999).

Ali et al. (Ali, Kotp, & El-Naggar, 2010) studied the formation of modified M-S-H by observing the effect of 0.1 M of HNO_3 on dried magnesium silicate samples prepared by mixing equal volumes (i.e. 0.3 mol/dm^3) of MgCl_2 and Na_2SiO_3 in a water bath for 3 hours at 80°C . The modified M-S-H revealed higher silica content, thermal stability and sorption potentiality compared to other samples with the addition of H_3PO_4 or NaOH. The sorption performance of magnesium silicate for Cu^{2+} , Cd^{2+} , Ni^{2+} and Fe^{3+} transition metal ions improved with increasing pH of the medium. Ciesielczyk et al. (Ciesielczyk, Krysztalkiewicz, & Jesionowski, 2007) performed modification of the surface of magnesium silicate through a “dry technique”, which involved the addition

of a specific amount of silane according to the desired amount of magnesium silicate. This modified the surface of magnesium silicate particles and improved their absorption ability with other active compounds by introducing functional groups to the surface. This modification influenced the diameter of the magnesium silicate particles by promoting an increase in the content of low diameter particles and increased the homogeneity of the sample, which are desirable for obtaining magnesium silicate with a reactive surface.

2.2.4. Research on cement formulations involving M-S-H

The slow hydration rate of MgO in cement mixes causes low initial strengths that can be increased with the addition of micro silica (Jin & Al-Tabbaa, 2014b). The incorporation of silica with MgO and water forms brucite, which reacts with the dissolved silica and produces M-S-H. This takes place in two stages involving the: (i) hydration of MgO to form brucite and the partial dissolving of SiO₂ to form silicon tetra-hydral networks, and (ii) reaction of brucite with dissolved silica to form M-S-H, while maintaining its layered structure (Golubeva et al., 2005). M-S-H is formed via the collection of silicon-oxygen layers on the magnesium-oxygen octahedral layer. The presence of brucite has a nucleation effect during this process.

When evaluating the effects of M-S-H within cement formulations, factors that directly influence the strength development are considered. Reactivity of MgO (i.e. which depends on the calcination duration and temperature used during its production, the particle size, and the presence of impurities, all determining the amount of brucite available for reaction) and the dissolution of silica (i.e. influenced by the particle size and quantity and the pH of the system (Iler, 1979)), are the major factors on the formation rate and degree of M-S-H. Jin and Al-Tabbaa (Jin & Al-Tabbaa, 2013) showed that higher pH and reactivity of the precursors (i.e. MgO and silica) are beneficial in the complete consumption of brucite and formation of M-S-H gel, whose composition mainly depends on the Mg/Si ratio and curing temperature (Jiangxiong Wei et al., 2011b).

Zhang et al. (T. Zhang et al., 2014b) investigated the addition of water reducers such as sodium hexametaphosphate (NaHMP) to MgO and silica fume mixes to accommodate for the high water demand of MgO. These water reducers improved the fluidity as well as the reaction degrees of MgO-silica pastes. The addition of 1% NaHMP significantly improved the mechanical performance of the M-S-H mixes formed, resulting in strengths as high as 70 MPa in 90 days. These results were achieved at an MgO to silica fume ratio of 2:3, which could be optimized further. Brucite remained in the system even after 285 days and continued to react with silica fume to produce M-S-H in the presence of sufficient water.

Cement matrices utilized in waste encapsulation applications are designed to have low permeabilities in order to limit contaminant mobility and prevent their penetration into the crystal structures of the hydrated cement products. For nuclear waste management, this is effective only when the internal pH of the cement matrix is high (i.e. ~10) (Bagosi & Csetenyi, 1998; Batchelor, 2006; D. M. R. Brew & F. P. Glasser, 2005; Shrivastava, Verma, & Wattal, 1995). The formation of M-S-H gel from a mixture of MgO and silica fume can counteract the effect of alkali impurities to maintain an overall pH in equilibrium with that of the cement matrix (i.e. ~10.5) (T. Zhang et al., 2011a). Therefore, cements with high silica fume and MgO contents can be successfully utilized in the encapsulation of metal wastes and immobilization of lead-contaminated soils to prevent the diffusion of lead in the surrounding environment (Ono & Wada, 2006). MgO incorporated in soils takes advantage of the soil moisture, yielding brucite. It can also react with silicic acid to form phyllosilicates under normal temperatures, which can fix lead within their interlayer spaces or octahedral sites.

2.2.5. Alternative silica sources for M-S-H production

The properties of raw materials, such as MgO and SiO₂, are one of the main factors controlling the strength development of M-S-H formulations. Most previous studies

(Jin & Al-Tabbaa, 2014b; Z. Li et al., 2014c; T. Zhang et al., 2014b) report the use of reactive MgO in combination with microsilica (MS) as the main silica source that reacts with Mg-phases to form M-S-H in cementitious mixes. While it is known that MgO sources with a higher reactivity lead to increased reaction degrees and hence rapid strength gain (Jin & Al-Tabbaa, 2013), the effect of different silica sources on the performance of M-S-H based mixes has not been investigated fully until now.

The chemical composition and physical properties of the silica source, which are controlled by its production conditions, determine the extent of M-S-H formation, as well as its final properties. For instance, crystalline silica was reported to have a limited reaction with MgO, thereby resulting in low strengths (i.e. 4 MPa at 90 days) in MgO-SiO₂ mixes, whereas higher reaction degrees and associated strength development was observed in the case of amorphous silica (Jin & Al-Tabbaa, 2014b). The limited strength development in the former case was associated with the lack of interaction between MgO and crystalline silica, which led to even lower strengths than purely MgO-based samples.

In line with the general trend focusing on enhancing the sustainability of cement-based mixes, the use of alternative materials in MgO-SiO₂ systems must be explored for the development of formulations with lower environmental impacts. Other than the commonly used MS, supplementary cementitious materials (SCMs) such as pulverized fuel ash (PFA) can be used as a silica source to react with Mg-phases and result in the formation of M-S-H. However, the use of PFA or similar SCMs can present some challenges as their chemical composition and properties vary from one source to another, resulting in the formation of phases other than M-S-H such as hydrated calcium silicate and carbonate gel due to the impurities present within PFA (T. Zhang, Du, Sun, He, & Wu, 2016). Although the use of PFA can be advantageous from an environmental standpoint, the variations in its composition and properties can limit strength development and result in lower strengths than samples containing SF.

Rice husk ash (RHA), which is a waste material obtained via the burning of rice hulls, is an alternative source that can be considered in the production of M-S-H due to its high SiO_2 content soluble in alkaline conditions and low environmental impact. Previous approaches involved the disposal of this material into water streams or its use as a fuel to power steam engines, which have other environmental implications. To alleviate this problem, many studies (Chao-Lung, Le Anh-Tuan, & Chun-Tsun, 2011; Gemma Rodríguez De Sensale, 2010; Ganesan, Rajagopal, & Thangavel, 2008; Zain, Islam, Mahmud, & Jamil, 2011) have investigated the use of RHA as a SCM in concrete mixes. In addition to presenting advantages in terms of mechanical performance, RHA enhanced the durability of concrete samples by contributing to the increase in density via its pozzolanic activity. Furthermore, the utilization of RHA in concrete formulations resulted in samples with lower environmental impacts due to the waste nature of RHA, meanwhile reducing the amount of waste going to landfills, the contamination of clean water sources from the uncontrolled disposal of RHA, and the CO_2 emissions associated with the use of rice hulls as a fuel.

Within the cement context, the properties of RHA depend on the raw materials and conditions used in its production. The production of RHA involves the burning of rice husks, which can take place via uncontrolled or controlled combustion. Uncontrolled combustion, usually lasting for longer durations, often results in a crystalline product (e.g. cristobalite or tridymite) with a high residual carbon content and a blackish color, which makes the resulting RHA unsuitable for any pozzolanic reaction. Alternatively, controlled combustion leads to the production of a higher quality RHA with a high amorphous SiO_2 content. Therefore, the quality (i.e. crystallinity/amorphous phase content) and therefore the suitability of the resulting RHA as a cementitious material depends on the burning conditions and the source of the rice husk (Chao-Lung et al., 2011). In this regard, the use of amorphous RHA improves the performance of cement-based mixes mostly due to its pozzolanic effect, whereas crystalline RHA mainly provides a filler effect (Gemma Rodríguez De Sensale, 2006; Isaia, Gastaldini, & Moraes, 2003).

2.3. Carbonation of MgO-based formulations

Differing from MgO-SiO₂-H₂O systems, carbonated MgO systems rely on the formation of hydrated magnesium carbonates (HMCs) for strength gain. This usually initiates with the hydration reaction of MgO into brucite, followed by the carbonation reaction to form a range of HMCs, as shown in Equations 2.6-2.10. The extent of the carbonation reaction, along with the morphology of these carbonate phases control the mechanical performance of carbonated MgO systems. Strength development of these binders is associated with the increase in sample density as carbonation is an expansive process that reduces the overall pore volume (i.e. the formation of HMCs causes a significant expansion and increases the solid volume by a factor of 1.8-3.1) and evolution of microstructure as the morphology and binding strength of the carbonate crystals contribute to the network structure.

As carbonation is the main mechanism for strength gain within these systems, the diffusion of CO₂ into the sample matrix plays a key role in the final performance. This necessitates the provision of the necessary porosity to enable CO₂ ingress, which can be achieved via a carefully planned mix design. Studies focusing on carbonated systems have generally proposed the use of 4-40% MgO as the main binder, accompanied with fine and/or coarse aggregates, along with fly ash or slag in some formulations (Dung & Unluer, 2016, 2017c; M Liska & Al-Tabbaa, 2008; Martin Liska & Abir Al-Tabbaa, 2009; Martin Liska, Al-Tabbaa, Carter, & Fifield, 2012a; M. Liska, L. Vandeperre, & A. Al-Tabbaa, 2008; Pu & Unluer, 2016). Although higher cement contents generally lead to higher strengths, this is associated with increased cost and environmental impacts. Therefore, achieving a balance amongst the

mechanical, economical and sustainability aspects of the proposed mix designs is important. Independent of the cement content, these studies have shown that subjecting MgO samples to natural atmospheric exposure conditions containing ambient CO₂ levels (0.04%) are not sufficient for the carbonation reaction to take place and provide high strengths even after several months (M Liska et al., 2008; Ruan & Unluer, 2017), therefore highlighting the need for accelerated carbonation conditions involving the use of elevated CO₂ concentrations (i.e. 5-20% in most cases). The use of these accelerated CO₂ concentrations was shown to enable compressive strengths as high as ~60 MPa after curing MgO-based concrete samples under 10% CO₂ for 28 days (Dung & Unluer, 2016).

While the use of elevated CO₂ concentrations increases the rate and degree of carbonation to some extent, the presence of uncarbonated brucite is a common occurrence in carbonated MgO systems as the penetration depth of CO₂ is limited towards the sample core (Pu & Unluer, 2016). One of the main reasons for this is the precipitation of carbonation products on the outer surface, which prevents further carbonation of Mg(OH)₂, thereby limiting carbonation and associated strength development, and resulting in an inefficient use of MgO as a binder. Since uncarbonated brucite does not significantly contribute to strength development by itself due to its poor binding capacity, the conversion of brucite or unhydrated MgO into strength providing phases such as HMCs or M-S-H can be enabled via the development of a combined system involving the presence of M-S-H as well as a carbonate network.

2.4. Performance under aggressive environments

In addition to their strength development and associated reaction mechanisms, the durability of MgO-SiO₂ samples in the long term need to be thoroughly assessed in order to enable their use on a large scale. Previous studies (Jia et al., 2016; T. Zhang, Liang, et al., 2016) reported the formation of shrinkage cracks in MgO-SiO₂

samples, which was overcome by the inclusion of sand in the mix composition. Other than these, there are no studies in the literature on the durability aspects of MgO-SiO₂ samples. A few studies (X. Li, 2013; Martin Liska & Al-Tabbaa, 2012) focusing on the durability of MgO samples under acid and sulfate conditions have reported the superior performance of samples with MgO over samples containing only PC. The higher performances of mixes containing MgO were attributed to the hydration product of MgO, i.e. brucite, not entering any detrimental reaction with acids or sulfates (Martin Liska & Al-Tabbaa, 2012). However, these studies did not involve any mixes containing SiO₂ and mainly focused on carbonated MgO samples or blends of PC and ground granulated blast furnace slag (GGBS) with MgO. Understanding the long-term performance of MgO-SiO₂ samples should also involve a comparison to existing PC-based samples, on which there is a wide range of literature.

Differing from MgO-SiO₂ systems, PC consists of four main phases, namely tricalcium silicate (C₃S), dicalcium silicate (C₂S), tricalcium aluminate (C₃A) and tetracalcium aluminoferrite (C₄AF). Calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) are the main hydration products observed in PC-based samples, whose hydration leads to a high internal pH (12.5-13). Constant access to a high humidity or water curing plays a vital role for the strength development of PC samples as the continuation of the hydration reaction requires humidity. Water cured samples have been reported to perform up to 23% better than air cured samples (Pierre-Claude Aitcin & Denis, 1994).

When PC samples are exposed to carbonation, CO₂ penetrates and dissolves in the pore solution, producing HCO₃⁻ and CO₃²⁻ ions, which lowers the pH. Dissolution of Ca(OH)₂ releases Ca²⁺ ions, which combines with CO₃²⁻ ions to form CaCO₃. The volume of CaCO₃ is larger than that of CH and thus carbonation may result in lower porosity and increased compressive strength, depending on the mix design and curing conditions (Chi, Huang, & Yang, 2002). However, carbonation can also lead to the decalcification of C-S-H, which results in carbonation shrinkage and formation

of cracks (Borges, Costa, Milestone, Lynsdale, & Streatfield, 2010). Additionally, the reduction in pH due to carbonation leads to the depassivation of the protective layer around steel reinforcement, thereby causing corrosion (Alonso, Andrade, Castellote, & Castro, 2000).

When PC samples are subjected to sulphate attack, formation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is observed due to reaction of CH with SO_4^{2-} ions (Neville, 2004). In addition to gypsum, ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) can also form via the reaction between gypsum and C_3A or via the reaction of sulphate ions with calcium aluminate hydrate (C-A-H) (Mostofinejad, Nosouhian, & Nazari-Monfared, 2016). Formation of gypsum and ettringite is an expansive process, which compromises volume stability and results in cracks and strength reduction (Rozière, Loukili, El Hachem, & Grondin, 2009). Alternatively, one of the main outcomes of chloride attack is the corrosion of reinforcement bars, which leads to significant problems in the performance and aesthetic properties of reinforced concrete structures (Shi, Xie, Fortune, & Gong, 2012). However, chloride ions by themselves are not as detrimental as other environments such as those involving sulfates (Glasser, Marchand, & Samson, 2008). Exposure of PC samples to chloride may result in the formation of Friedel's salt ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$) and calcium oxychlorides (Glasser et al., 2008), which causes hydraulic pressure in cement matrix (Sutter, Dam, Peterson, & Johnston, 2006). In the presence of Mg^{2+} ions, precipitation of brucite ($\text{Mg}(\text{OH})_2$) and formation of M-S-H due to reaction of MgCl_2 with decalcified C-S-H can also be observed (Jakobsen, De Weerd, & Geiker, 2016), which can lead to a porous structure (Maes & De Belie, 2014).

Chapter 3: MATERIALS AND EXPERIMENTAL PROCEDURES

3.1. Introduction

This chapter presents the materials, test methods and the experimental procedures used to obtain the results.

3.2. Materials

3.2.1. Magnesium Oxide

The reactive magnesium oxide (MgO) used in sample preparation was “calcined magnesite 92/200” (supplied by Richard Baker Harrison Ltd., United Kingdom). Chemical composition and physical properties of MgO are listed in Table 3.1, as obtained from the supplier. XRD plot showing the crystalline peak pattern of MgO is presented in Figure 3.1. In addition to the MgO peaks at 37°, 43°, 62°, 75°, 79° 2 Theta (2θ), a magnesite (MgCO₃) peak is observed as an impurity at 33° 2θ. The microstructure of MgO (Figure 3.2) consisted of aggregated grains of microparticles, which was consistent with those observed in other studies (E. Alvarado, L. M. Torres-Martinez, A. F. Fuentes, & P. Quintana, 2000a; Mo et al., 2010). The reactivity of MgO was measured as 50 seconds according to acetic acid reactivity test (Shand, 2006). The standard consistency of MgO was determined as 0.64.

Table 3.1 Chemical composition and physical properties of MgO

MgO	
Chemical composition	
MgO	>91.5%
CaO	1.6%
SiO ₂	2.0%
Al ₂ O ₃	<0.7%
LOI	4%
Physical properties	
Particle size (%)	<74 μm 95% min

Figure 3.1 XRD plot of MgO

Figure 3.2 FESEM image of MgO

3.2.2. Microsilica

The microsilica (MS) used was 940U (supplied by Elkem Singapore Materials Pte Ltd.). The chemical composition and physical properties of MS reported by the supplier is shown in Table 3.2. The XRD plot for MS is presented in Figure 3.3, showing an amorphous broad band at around $22^\circ 2\theta$, which is characteristic for amorphous SiO_2 . The morphology of MS was composed of spherical SiO_2 particles as shown in Figure 3.4.

Table 3.2 Chemical composition and physical properties of MS

MS	
Chemical composition	
MgO	-
CaO	-
SiO_2	>90%
Al_2O_3	-
LOI	<3%
Physical properties	
Particle size (%)	>45 μm 1.5% max

Figure 3.3 XRD plot of MS

Figure 3.4 FESEM image of MS

3.2.3. Portland cement

Portland cement (PC) used in this thesis was obtained from Lafarge Cement (Singapore). The chemical composition and physical properties of PC as obtained from the supplier are presented in Table 3.3.

Table 3.3 Chemical composition and physical properties of PC

PC	
Chemical composition	
MgO	0.9%
CaO	66.2%
SiO ₂	20.9%
R ₂ O ₃	10.0%
K ₂ O	0.5%
Na ₂ O	0.1%
LOI	1.1%
Physical properties	
Specific gravity (g/cm ³)	3.1

3.2.4. Sodium hexametaphosphate

A superplasticizer (SP), namely sodium hexametaphosphate (SHMP) (supplied by VWR Singapore Pte Ltd., Singapore) was used to provide the desired workability of the prepared mixes and to avoid agglomeration of MgO and MS particles. Figure 3.5 shows the chemical structure of SHMP, which is a hexamer of Na(PO₃)₆. It appears as white crystals (Figure 3.6) and is soluble in water.

Figure 3.5 Structure of SHMP

Figure 3.6 SHMP crystals

3.2.5. Natural aggregates

Saturated surface dry (SSD) gravel provided by Buildmate (Singapore) with a particle size of 4.7–9.5 mm and a density of 2.61 kg/m^3 was used to form the aggregate profile in the concrete samples prepared.

3.2.6. Crystalline RHA

Crystalline RHA (RHA-c) was obtained from Dinxings (Malaysia). Chemical composition and physical properties of RHA-c are listed in Table 3.4. The XRD plot of RHA-c is presented in Figure 3.7. The composition of RHA-c was composed of crystalline peaks of cristobalite, a polymorph of quartz. The morphology of RHA-c (Figure 3.8) was made up of larger sized inhomogeneous particles that agglomerated into a dense structure. The RHA-c powder is black in color (Figure 3.9) due to its high carbon content and has a relatively lower SSA value of $8.6 \text{ m}^2/\text{g}$.

Table 3.4 Chemical composition and physical properties of RHA-c

Component/ Content (%)	RHA-c
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MgO	0.5
CaO	0.4
SiO ₂	>75.0
Al ₂ O ₃	0.06
C	18.3
P ₂ O ₅	0.6
Fe ₂ O ₃	0.09
K ₂ O	2.3
SO ₃	0.03
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Specific surface area (m ² /g)	8.6
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LOI (%)	1.3
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Figure 3.7 XRD plot of RHA-c

Figure 3.8 FESEM image of RHA-c at 2,000 magnification

Figure 3.9 RHA-c powder

3.2.7. Amorphous RHA

RHA with a significant amorphous SiO_2 content (RHA-a) was obtained from NanoSiltech (Malaysia). Chemical composition and physical properties of RHA-a are listed in Table 3.5. XRD plot of RHA-a (Figure 3.10) contained a combination of low intensity crystalline peaks that matched well with the major peaks of cristobalite, as well as an amorphous band at around $15\text{-}27^\circ 2\theta$, which corresponded to amorphous silica, similar to what observed in MS. Figure 3.11 (a) and (b) shows the morphology of RHA-a under low and high magnification, respectively. Under low magnification the cellular structure of RHA and under high magnification agglomerated grains stacked together was observed. The RHA-a powder (Figure 3.12) has grey color which included traces of black colored carbon particles inside. The SSA of RHA-a is $24.1 \text{ m}^2/\text{g}$.

Table 3.5 Chemical composition and physical properties of RHA-A

Component/ Content (%)	RHA-a
MgO	0.7
CaO	0.5
SiO ₂	>79.0
Al ₂ O ₃	0.1
C	15.3
P ₂ O ₅	1.4
Fe ₂ O ₃	0.1
K ₂ O	2.4
SO ₃	0.3
Specific surface area (m ² /g)	24.1
LOI (%)	5.2

Figure 3.10 XRD plot of RHA-a

Figure 3.11 FESEM image of RHA-a (a) under low magnification (X500) and (b) under higher magnification (X30,000)

Figure 3.12 RHA-a powder

3.3. Sample Preparation

3.3.1. MgO-SiO₂ based paste samples

Sample preparation initiated with dissolving SHMP in predetermined amount of water, after which MgO was slowly added in during mixing. MS was then gradually introduced into the mix at the determined MgO:MS ratio. Mixing continued until a thoroughly mixed and a highly workable paste was obtained. The prepared paste was then poured into 50x50x50 mm cubic molds, which were kept in a sealed moist condition for 24 hours before being demolded. The demolded samples were cured in the environments stated in the results sections, depending on the set of experiments, for different durations until they are tested for their compressive strength. For the samples prepared in Chapter 5 where RHA powders were utilized as the SiO₂ source, exact same procedure was followed by replacing the MS with the RHA source.

3.3.2. MgO and MgO-SiO₂ based concrete samples

In chapter 6, MgO and MgO-SiO₂ based binders were used in the preparation of concrete samples that were composed of 40% binder (i.e. to provide binding in the absence of fine aggregates, which were omitted from the mix design to avoid contamination with quartz and provide an accurate quantification of hydrate and carbonate phases during microstructural analysis) and 60% coarse aggregates, by mass. First, the binder phase was prepared as explained in section 3.3.1. After a truly homogenized and thoroughly mixed paste was obtained, coarse aggregates were introduced into the mix. The prepared mix was cast into 50x50x50 mm cubic molds, compacted using a vibration table and the surface was trowel finished. The concrete samples were kept in a sealed moist condition for 24 hours before being demolded, after which the samples were placed into respective curing conditions. The demolded MgO-SiO₂ based concrete samples are presented in Figure 3.13.

Figure 3.13 50 mm cubic MgO-SiO₂ based concrete samples

3.3.3. PC based concrete samples

PC based concrete samples were prepared in a similar manner to MgO-SiO₂ based samples, in which PC was slowly introduced into the predetermined amount of water and carefully mixed to ensure complete homogeneity. Coarse aggregates were introduced into the mix after the binder component was thoroughly mixed.

3.4. Methodology

3.4.1. Acid reactivity

Acetic acid reactivity test was applied to determine the reactivity of MgO. The test procedure involved adding 5 g of MgO into 300 mL of distilled water while mixing at 2500 rpm. 8-10 drops of phenolphthalein was added during this process as a colour indicator. While mixing, 100 ml of 1.0 N acetic acid (CH₃COOH) was quickly added to the slurry and the stop watch was started. The time it took the solution to gain a pink colour was reported as the reactivity. The test was conducted in triplicates per sample.

During this test, MgO hydrates and releases the hydroxide anion (OH⁻), whereas the acetic acid dissociates in water and releases the hydrogen cation (H⁺) as shown in

Equations 3.1 and 3.2, respectively.

Phenolphthalein indicator indicates a pink colour at a pH range of 10-13. Once MgO releases sufficient amounts of OH^- to neutralise the H^+ and increase pH, the solution turns pink. Therefore the reactivity test indicates the length of time MgO powder needs to react with water. The longer time taken to change the colour of the solution to pink refers to MgO with a lower reactivity.

3.4.2. Standard consistency

The standard consistency measurement was performed according to ASTM C187-98 via a standard Vicat apparatus supplied by ELE Pte Ltd. (Singapore) as shown in Figure 3.14. The pastes were prepared with different water to solid ratios to determine the exact consistency value corresponding to a needle penetration depth of 10 ± 1 mm as specified by the standard. The test was conducted once per sample.

Figure 3.14 The Vicat apparatus used for SC measurements

3.4.3. Particle size distribution (PSD) of powders

The PSD of the raw materials was determined via a Malvern Mastersizer 2000 (Figure 3.15). Before the analysis, the powders were added into water and mixed thoroughly to prepare a homogenous solution. A few drops of this solution were placed in the equipment for the PSD analysis. The test was conducted once per sample.

Figure 3.15 Malvern Mastersizer 2000 instrument used for PSD analysis of MgO and MS powders

3.4.4. Workability

The workability of the prepared MgO-SiO₂ pastes was measured using a flow table incorporating an impact method in accordance with ASTM C1437-15. During this test, impact was applied 25 times within 15 seconds to spread the paste. Four diameter values perpendicular to each other were measured and the average of these four values was reported as the final workability value. Figure 3.16 shows a paste after the impact method was applied.

Figure 3.16 Application of the impact method on a paste on the flow table

3.4.5. pH measurements

For the measurements presented in Chapters 4 and 7, the pH values of samples were determined at different ages by crushing and grinding the samples and dispersing the fragments in water. Following an hour of mixing, the solids were filtered through vacuum and the pH was measured by using a Mettler Toledo pH meter (Figure 3.17 (a)) with an accuracy of ± 0.01 . All the measurements were conducted in triplicates and the average values were recorded.

For the measurements presented in Chapter 5, the pH values of the raw material solutions and sample solutions were determined at different ages (i.e. 0, 1, 2, 7, 14 and 28 days) by dispersing the powders in water. For sample solutions, raw materials were mixed at the same proportions that are employed for sample preparation. The solutions were continuously mixed except during the measurements are taken and the pH was measured by using a Horiba F-52 pH meter (Figure 3.17 (b)) with an accuracy of ± 0.01 . All the measurements were conducted in triplicates and the average values were recorded.

(a)

(b)

Figure 3.17 Instrument used for measuring pH (a) Mettler Toledo pH meter and (b) Horiba F-52 pH meter

3.4.6. Isothermal calorimetry

The heat flow and cumulative heat evolved due to the hydration of samples were determined under isothermal conditions at by an I-Cal 2000 High Precision Calorimeter (Figure 3.18) in accordance with ASTM C1702 – 15a (2015). To initiate the analysis, dry powder was added to water, which was previously placed into calorimeter in order to obtain the water at the same temperature as the determined calorimetry temperature. The prepared mix was instantaneously placed into the isothermal calorimeter channel to measure the heat of hydration at the designated temperature. The test was conducted once per sample.

Figure 3.18 Equipment used for isothermal calorimetry

3.4.7. Compressive strength

The compressive strengths (CS) of the prepared samples were measured by uni-axial loading. The equipment used for this purpose was a Toni Technik Baustoffprüfsysteme machine (Figure 3.19), operated at a loading rate of 55 kN/min. For each experiment 50 mm cubic samples were prepared, and average value and standard deviation of the tested samples in each data set were reported. For each data point 6 samples were tested.

Samples extracted from the cubes crushed during compressive strength testing were stored in acetone for at least 3 days to stop hydration, followed by vacuum drying in preparation for XRD, TG/DTG, FTIR and FESEM analyses. The extraction of powders for microstructural analyses was performed by following the quartering method, which involved powders from different depths in the selection of the final powder. This measure was taken to ensure the extraction of samples that were truly representative of the entire system. For microstructural analyses the samples were tested one time.

Figure 3.19 Equipment used for CS testing

3.4.8. X-ray diffraction

Two different X-ray diffraction (XRD) equipment were used in this thesis. The first equipment listed below was used for the results presented in Chapter 4 and the second equipment was used for the results presented in Chapters 5, 6 and 7. Although the models of the two equipment were the same, the detectors used were different.

1) Bruker D8 Advance machine using Cu $K\alpha$ radiation (40 kV, 30 mA) with a scanning rate of 0.04° 2θ /step from 10 to 80° 2θ was used for the collection of XRD data. The equipment used for this purpose shown in Figure 3.20 (a) was located in the Environmental Laboratory of the School of Civil and Environmental Engineering (CEE).

2) Bruker D8 Advance instrument using Cu $K\alpha$ radiation (40 kV, 30 mA) with a scanning rate of 0.02° 2θ /step from 10 to 80° 2θ was used for the collection of XRD data. The machine, shown in

Figure 3.20 (b), was located in the Facility for analysis characterisation testing and simulation (FACTS) Laboratory of the School of Materials Science and Engineering (MSE).

Figure 3.20 Equipment used for XRD analysis (a) XRD instruments in CEE and (b) XRD instrument in MSE

3.4.9. XRD-RIR

The Reference Intensity Ratio (RIR) technique (Hubbard & Snyder, 1988; Johnson & Zhou, 2000; Snyder, 1992) was applied for the quantitative analysis of the crystalline phases by making use of a standard phase with a known proportion, whose integrated intensity was compared to that of a phase of interest. The internal standard used for quantification purposes was fluorite (CaF_2) included at 5 wt.% (Klug & Alexander, 1954). Calibration curves for MgO and $\text{Mg}(\text{OH})_2$, the two main components used for quantitative analysis, are straight lines through the origin i.e. $y = kx$, where x is the RIR of the phase analysed and y is the weight fraction of the component investigated. The value of k is 0.2886 for MgO and 0.3651 for $\text{Mg}(\text{OH})_2$ (Klug & Alexander, 1954). The RIR was acquired by dividing the integrated intensity of the strongest line of the phase with that of the standard.

3.4.10. Field emission scanning electron microscopy

Observation of the sample microstructures were performed via field emission scanning electron microscopy (FESEM). The vacuum dried samples were coated with platinum before conducting FESEM. The morphologies of the samples were investigated by a JEOL JSM-7600F equipment (Figure 3.21).

Figure 3.21 Equipment used for FESEM analysis

3.4.11. Thermogravimetric analysis

Two different thermogravimetric analysis (TG) equipment were used in this thesis. The first equipment listed below was used for the results presented in Chapter 4 and the second equipment was used for the results presented in Chapters 5, 6 and 7.

1) Perkin Elmer Diamond TG/DTA equipment was used to conduct TG/DTA from 40 to 900 °C with a heating rate of 10 °C/min under nitrogen flow. The equipment used for this purpose shown in Figure 3.22 (a) was located in the School of Chemical and

Biomedical Engineering (SCBE).

2) Perkin Elmer TGA 4000 equipment was used to conduct TG/DTG from 30 to 900 °C with a heating rate of 10 °C/min under nitrogen flow. The machine, shown in Figure 3.22 (b), was located in the Environmental Laboratory of the School of Civil and Environmental Engineering (CEE).

(a)

(b)

Figure 3.22 Equipment used for TGA (a) Perkin Elmer Diamond TG/DTA and (b) Perkin Elmer TGA 4000

3.4.12. Derivative thermogravimetric analysis (DTG)

The quantification of the formed phases within selected samples was performed via the deconvolution of the DTG curves and the calculation of the area corresponding to different decomposition reactions under each deconvoluted curve.

3.4.13. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) analyses were conducted using Potassium bromide (KBr) pellets with a KBr to sample ratio of approximately 150. Two different FTIR equipment were used in this thesis. The first equipment listed below was used for the results presented in Chapter 4 and the second equipment was used for the results presented in Chapter 5.

- 1)** Perkin Elmer FTIR Spectrometer Spectrum GX (Figure 3.23 (a)) was used to obtain the FTIR spectra of samples. The infrared spectra were the result of averaging 32 scans over a range of $4000\text{--}400\text{ cm}^{-1}$, with a resolution of 4 cm^{-1} .
- 2)** Perkin Elmer Frontier FTIR Spectrometer (Figure 3.23 (c)) was used to obtain the FTIR spectra of samples. The infrared spectra were the result of averaging 32 scans over a range of $4000\text{--}400\text{ cm}^{-1}$, with a resolution of 4 cm^{-1} .

(a)

(b)

(c)

(d)

Figure 3.23 Equipment used for FTIR (a) Perkin Elmer FTIR Spectrometer Spectrum GX, (c) Perkin Elmer Frontier FTIR Spectrometer, and (b) and (d) the hydraulic presses used for preparation of FTIR pellets

Chapter 4: INFLUENCE OF MIX DESIGN AND CURING CONDITIONS ON SAMPLE PERFORMANCE AND MICROSTRUCTURE

This chapter consisted of two main sections which focused on the investigation of i) mix design parameters, and ii) curing conditions for MgO-SiO₂ formulations. The initial part of the study focused on the assessment of the mechanical performance of MgO-SiO₂ pastes with different mix designs involving variations in the initial binder composition (i.e. Mg/Si ratios) and water/binder (w/b) ratio. This was followed by the second part of the study which focused on the evaluation of the effect of curing conditions on the compressive strength and microstructural development of MgO-SiO₂ pastes.

4.1. Influence of key mix design parameters on the performance of MgO-SiO₂ samples

4.1.1. Introduction

This research focused on systematic investigation of the effect of various mix parameters on the performance of MgO-SiO₂ based binders. MgO-SiO₂ pastes with different initial binder composition (i.e. Mg/Si ratios), w/b ratio and SHMP content were assessed based on their compressive strength and workability. The findings emerging from this study were aimed to provide guidance in the preparation of an ideal MgO-SiO₂ mix design, based on mechanical performance.

4.1.2. Mix details

The first part of the experimental study focused on the investigation of the effect of binder composition on sample performance. To determine the optimum binder composition, the mixes, whose compositions are presented in Table 4.1, were prepared and tested for their compressive strengths at 28 days. Within this batch, the MgO and MS contents varied between 30-70%. Another set of samples only

containing MgO (MgO100) was prepared as the control sample for comparison purposes. Two different w/b ratios (0.4 and 0.5) were utilized for all mixes, while the SHMP content was kept constant at 1% of the total binder content, to assess the influence of water content on strength development. The prepared 50x50x50 mm cubic paste samples were cured under sealed moist conditions (30 ± 2 °C, $95\pm5\%$ RH) until they were tested.

Table 4.1 Mix composition of the MgO-SiO₂ pastes

Sample	MgO (wt.%)	MS (wt.%)	w/b	SHMP content	
MgO30-0.4	30	70	0.4	1% by weight of the total binder content	
MgO40-0.4	40	60			
MgO50-0.4	50	50			
MgO60-0.4	60	40			
MgO70-0.4	70	30			
MgO100-0.4	100	0			
MgO30-0.5	30	70	0.5		
MgO40-0.5	40	60			
MgO50-0.5	50	50			
MgO60-0.5	60	40			
MgO70-0.5	70	30			
MgO100-0.5	100	0			

The second part of the experimental study focused on the role of SHMP content on sample performance. For this purpose, the mix design achieving the highest strength in the first experimental part (MgO60-0.4) was selected for further analysis. SHMP content was varied between 0-10% of the total binder content within this mix design, while the w/b was kept constant at 0.4. The workability of all pastes prepared during the second part were assessed via flow table measurements by taking the average of four flow diameters in accordance with ASTM C1437-15.

4.1.3. Results and Discussion

The strength development of MgO-SiO₂ formulations are dependent on the formation of M-S-H, whose amount and properties are influenced by the initial mix design (i.e. MgO/SiO₂ ratio and water content). The effect of binder composition (i.e. MgO/SiO₂ ratio), along with the w/b ratio, on sample performance are revealed by the 28-day compressive strengths in Figure 4.1. Generally, an increase in strength was observed with a reduction in the w/b ratio from 0.5 to 0.4. This was associated with the lower porosity of the samples containing lower water contents, which led to higher strengths. In terms of the binder composition, an increase in strength from 45 to 57 MPa was revealed as the MgO content increased from 30 to 60% within samples containing w/b ratios of 0.4. Any further increase in the MgO content to $\geq$ 70% led to a noticeable reduction in strength to 40 MPa and lower. A similar trend was observed at w/b ratios of 0.5, albeit the cut-off was observed at an MgO content of 50%, after which the 28-day strength reduced from 53 to 44 MPa. This was associated with the achievement of a more resistant structure in the MgO/SiO₂ range of 0.8-1.2.

Figure 4.1 Compressive strength of MgO-SiO₂ pastes at 28 days

When compared to formulations involving the simultaneous use of MgO and SiO₂, the sole use of MgO in the MgO100 sample revealed the lowest strengths amongst all samples at both w/b ratios. This was due to the lower binding strength provided by the formation of brucite in the MgO100 sample, in comparison to M-S-H in MgO-SiO₂ formulations. Out of all the samples prepared in this study, those involving a combination of 60% MgO and 40% SiO₂ at a w/b ratio of 0.4 achieved the highest 28-day strength of 57 MPa. Therefore, the MgO60-0.4 sample was used in the subsequent studies focusing on the influence of SHMP content (within paste mixes).

Figure 4.2 shows the influence of SHMP content on the workability (i.e. indicated in terms of the flow diameter) of the MgO60-0.4 mix. An increase in workability was observed with an increase in the SHMP content up to 2%, after which the trend reversed. Any increase in the SHMP content beyond 2% caused a reduction in the workability of the MgO-SiO₂ mix, which indicated almost no movement as the SHMP content reached up to 10%. This was associated with the formation of a protective layer of $[6\text{MgOH}^+(\text{PO}_3)_6]^{6-}$ (insoluble), which can form a bulky structure and reduce workability at SHMP contents of > 2% (Jia et al., 2016).

Figure 4.2 Flow diameter of the MgO60-0.4 mix containing different amounts of SHMP

Figure 4.3 shows the FESEM images of the best performing MgO-SiO₂ samples at 28 days. The formation of a continuous layer of M-S-H covering other particles, together with small amounts of brucite (i.e. lamellar aggregates of platelets) and unreacted spherical SiO₂ particles, were observed. The continuous layer established by M-S-H, which formed as a result of the reaction between MgO/Mg(OH)₂ and SiO₂, led to the binding and densification of the microstructure, explaining the strength development of MgO-SiO₂ formulations.

Figure 4.3 FESEM images showing M-S-H formation within MgO-SiO₂ formulations

4.1.4. Conclusions

The parameters for initial MgO/SiO₂ ratio in relation to w/b ratio, and SHMP content were concluded and these values were utilized for the rest of the thesis. At w/b of 0.4, paste mix with 60% MgO and 40% SiO₂; whereas at 0.5 w/b, paste mix with 50% MgO and 50% SiO₂ was chosen to be optimum for MgO-SiO₂ formulations. Additionally, it was concluded that SHMP content should be kept at maximum 2% of total binder weight.

4.2. Performance and microstructural development of MgO-SiO₂ binders under different curing conditions

4.2.1. Introduction

This research evaluates the influence of different curing conditions on the hydration process and formation of M-S-H; and identifies a connection between the enhanced M-S-H formation and mechanical performance of the developed binders. This was enabled by improving the reaction mechanisms via the adjustment of curing conditions. The effect of different curing conditions on the performance of MgO-SiO₂-H₂O formulations was evaluated through the progress of hydration and mechanical performance of the prepared samples. The amount and structure of the hydrate phases, as well as the microstructure of the prepared samples were analysed under various curing conditions. The hydration process was assessed by isothermal calorimetry and pH tests. The mechanical performance was evaluated by compressive strength testing at different durations up to 56 days. The formation of Mg(OH)₂ and M-S-H was investigated via X-ray diffraction (XRD) – reference intensity ratio (RIR), thermogravimetric/differential thermal analysis (TG/DTA) and Fourier transform infrared spectroscopy (FTIR), while the microstructural development of the prepared formulations was observed by field emission scanning electron microscopy (FESEM).

4.2.2. Mix details and curing conditions

Samples were prepared by dissolving SHMP in water, after which MgO was slowly added in during mixing. MS was then gradually added to the mix at an MgO:MS ratio of 1:1. The water/binder ratio was kept constant at 0.5 for all mixes. Mixing was continued until a thoroughly mixed paste was obtained. The prepared paste was then poured into 50x50x50 mm cubic moulds, which were kept in a sealed moist condition for 24 hours before being demoulded. The demoulded samples were cured in five different environments for up to 56 days, details of which are listed in Table 4.2. Samples S, A and W30 were cured at around 30 °C under a range of humidity

levels; whereas samples W60 and O were cured at 60 °C under water and in oven, respectively. The effects of these different curing conditions on the hydration, mechanical performance and microstructural development of each sample are discussed in detail in Section 4.2.3.

Table 4.2 Curing conditions used in this study

Sample	Curing conditions		
	Environment	Temperature (°C)	Relative humidity (%)
S	Sealed	30±2	95±5
A	Ambient	30±2	60±5
W30	Under water	30	-
W60	Under water	60	-
O	Oven	60	-

4.2.3. Results

4.2.3.1. Isothermal calorimetry

Figure 4.4 (a) and (b) show the heat flow and the cumulative heat evolved during the hydration of MgO pastes for up to 72 hours at 30 °C and 60 °C, respectively. The dissolution took place within a few minutes after mixing under both temperatures. The hydration process was accelerated at 60 °C as evident from the significantly higher exothermic peak than that observed at 30 °C. The heat flow curves indicated a rapid acceleration within the first 8 hours under 60 °C, followed by a much slower dissolution process as the heat flow slowly diminished. The drop in the heat flow of sample under 60 °C at as early as 8 hours could be attributed to the reaction

between the dissolved MgO and MS, as well as the reduction in the rate of MgO hydration. Although a lower hydration peak was observed initially at 30 °C, the hydration process continued for a longer duration as indicated by the heat flow pattern.

The cumulative heat curves of hydration under the two different temperatures are shown in Figure 4.4 (b). The higher heat content revealed during the first 45 hours under 60 °C was an indication of the higher degree of initial hydration when compared to 30 °C. Although the hydration process was accelerated at elevated temperatures (60 °C) in the early stages (≤ 45 hours), this trend did not continue in the longer durations. Samples hydrated at 30 °C revealed a higher amount of cumulative heat after 45 hours due to the continuation of the hydration reaction. The ceasing of hydration in the later ages at 60 °C could be due to the rapid formation of hydration products, which nucleated and grew on the MgO particles at early ages. This may have hindered any further contact between unhydrated MgO and water, thereby preventing the continuation of hydration (Mo et al., 2010). The gradual formation of brucite during the hydration process that took place at a slower rate at 30 °C may have enabled the dissolution of MgO and MS away from the unhydrated MgO, which could provide a higher amount of surface area available for continuous hydration.

(a)

(b)

Figure 4.4 Isothermal calorimetry results of pastes showing the (a) heat flow and (b) cumulative heat at 30 and 60 °C

4.2.3.2. pH

The pH measurements were conducted with the aim of assessing the degree of hydration reaction and the type of hydration products formed. The pH values of solutions involving samples cured for 3 and 28 days under different curing conditions are presented in Table 4.3 pH values of samples measured at 3 and 28 days. As the contents and properties of MgO and MS were kept constant in all samples, the change of pH was due to the variations in curing conditions and durations. The pH values of the samples were an indication of the type of hydration products formed. The initial pH values of all samples cured for 3 days varied between 10.5 and 11.2. This was consistent with the pH of a saturated brucite solution (~ 10.5), which can be slightly higher in the presence of impurities (e.g. CaO) within MgO. The pH results were in line with the findings of previous studies (Z. Li et al., 2014b; T. Zhang et al., 2011b), which reported an increase in the pH of MgO-silica mixes to ~ 11.2 during the first few (≤ 3) days due to the dissolution of MgO. This was followed by a decrease in the pH associated with the formation of M-S-H.

Samples W60 and O cured under 60 °C indicated the lowest pH values of 10.5-10.6 amongst all samples at 3 days. The lower pH values demonstrated by these samples were attributed to their rapid hydration and consumption of $\text{Mg}(\text{OH})_2$ by the dissolved MS, which was stimulated by the elevated temperatures used during their curing. Similarly, samples S, A and W30 cured under 30 °C demonstrated comparable pH values of 11-11.2 due to the similar rates of hydration at 3 days. Reduction of the pH values of samples S, A and W30 was observed going from 3 to 28 days, at the end of which all samples revealed pH values within the narrow range of 10.4-10.5. This change in the pH was attributed to the precipitation of brucite and the simultaneous formation of M-S-H. The 28-day pH values revealed by samples cured under 30 °C were equivalent to those achieved by the W60 and O samples at 3 days, confirming the increase in the initial hydration rate at elevated temperatures.

Table 4.3 pH values of samples measured at 3 and 28 days

Sample	pH	
	3 days	28 days
S	11.2	10.4
A	11.1	10.5
W30	11.0	10.4
W60	10.5	10.5
O	10.6	10.4

4.2.3.3. Compressive strength

The compressive strength results of all samples subjected to different curing conditions for up to 56 days are presented in Figure 4.5. Samples cured under sealed conditions demonstrated strengths as high as 50.4 and 53.1 MPa at 28 and 56 days, respectively. Early (3 day) strengths of up to 33.9 MPa were achieved by samples subjected to high temperatures (W60 and O). These results indicate the important role curing conditions (i.e. the relative humidity and temperature) play on the strength development of M-S-H systems.

The effect of relative humidity (60% vs. 95%) on strength development can be assessed via a comparison of samples subjected to ambient (A) and sealed (S) curing conditions. An obvious increase in the strength of S samples was observed when compared to those subjected to ambient curing. The difference in strength values became even more prominent in longer durations (≥ 14 days), at which S samples revealed the highest strength results. This could be attributed to the continuation of the hydration reaction under the high humidity provided by sealed curing. Samples subjected to ambient curing did not demonstrate any strength gain after 14 days. The introduction of

underwater curing at the same temperature (30 °C) in W30 samples led to a slight reduction in strength when compared to A and S samples. This could be because of the leaching of ions under water, which was also reported in previous studies (Jin & Al-Tabbaa, 2014b).

The effect of water curing and temperature was observed via a comparison of W30, W60 and O samples. The introduction of higher temperatures in W60 samples cured under water at 60 °C led to a significant increase in strength, revealing strengths as high as 33.9, 39.7 and 39.1 MPa at 3, 7 and 14 days, respectively. These were up to 226% (at 3 days) higher than the strengths of the corresponding W30 samples. A similar outcome was observed in O samples, whose 3-day strength results were 33.8 MPa (i.e. 89% and 225% higher than corresponding S and W30 samples). These results were in line with the isothermal calorimetry and pH results presented earlier, which highlighted the advantage of high temperature curing on the progress of hydration at early ages. The high temperatures used during the curing of W60 and O samples were mainly favourable for initial strength gain, after which both samples experienced a reduction in their strengths. This strength reduction was more pronounced for O samples, which demonstrated lower strengths after 3 days. This could be due to the evaporation of water and loss of the interlayer water of M-S-H when exposed to 60 °C. A similar outcome was observed in previous studies reporting the formation of shrinkage cracks when M-S-H samples were subjected to increased temperatures (Jia et al., 2016; T. Zhang, Liang, et al., 2016).

Figure 4.5 Compressive strength of all samples cured for up to 56 days

4.2.3.4. XRD

Figure 4.6 (a) and (b) show the XRD diffractograms of all samples cured for 3 and 28 days, respectively. Some of the main phases observed were MgO at 42.9° and 62.3° 2θ and brucite at 18.6° , 38.0° , 50.8° , 58.6° and 68.2° 2θ . The presence of MgO and brucite was an indication of the incomplete hydration reaction at both curing durations, highlighting the potential of these formulations to achieve further strength gain if their complete hydration was realized. Consistent with the strength results, the intensity of the MgO peaks were greatly reduced within S samples at 28 days as an indication of the higher degree of the utilization of MgO in the hydration reaction.

(a)

(b)

Figure 4.6 XRD diffractograms of all samples cured for (a) 3 days and (b) 28 days (M: MgO, B: Brucite, F: Fluorite)

The broad peaks at 17-28°, 32-39° and 58-62° 2 θ indicated the presence of amorphous M-S-H (M Tonelli et al., 2016). Although M-S-H broad peaks could be seen in all samples, these were most obvious for W60 and O samples at 3 days. The presence of M-S-H was diminished for O samples at 28 days, during which associated peaks were observed in all other samples. Table 4.4 shows MgO and brucite contents of all samples at 3 and 28 days quantified by XRD-RIR technique. At 3 days W60 sample has the lowest MgO content amongst all samples indicating a rapid hydration within the sample which was facilitated by elevated temperature coupled with the presence of water in the curing environment. All samples, except O sample, demonstrated a decrease in MgO content from 3 to 28 days which is an indication of continuation of hydration reaction. In line with this observation, brucite content of all samples increased from 3 to 28 days. The rate of increase in brucite content was not as high as the decrease in the MgO content between 3 and 28 days. The difference between these two values was attributed to formation of M-S-H, whose content is calculated using XRD-RIR results together with the TGA quantification results in Section 4.2.3.5.

Table 4.4 XRD-RIR quantifications for MgO and brucite at both 3 and 28 days

Phase	Curing duration (days)	Content quantified by XRD-RIR (%)				
		Sample				
		S	A	W30	W60	O
MgO	3	29.9	39.9	40.5	13.1	21.9
	28	17.6	31.7	31.7	9.2	35.7
Brucite	3	12.5	12.5	9.8	12.8	5.9
	28	14.6	14.6	15.5	12.9	6.4

4.2.3.5. TG/DTA

Figure 4.7 (a) and (b) show the TG/DTA plots of all samples cured for 3 and 28 days, respectively. Since all samples were subjected to vacuum drying for 7 days before testing, the total mass loss observed during this process corresponded to the decomposition of hydrate phases (i.e. brucite and M-S-H). The main steps involved during the thermal decomposition were (Jin & Al-Tabbaa, 2013; Lothenbach, Nied, L'Hôpital, Achiedo, & Dauzères, 2015; Nied, Enemark-Rasmussen, L'Hopital, Skibsted, & Lothenbach, 2016):

40-300 °C: Loss of interlayer water of M-S-H

300-750 °C: Dehydroxylation of brucite (300-450 °C) and separation of hydroxyl groups in M-S-H

750-850 °C: Dehydroxylation of silanol groups

(a)

(b)

Figure 4.7 TG/DTA plot of samples cured for (a) 3 days and (b) 28 days

The mass loss values demonstrated by all samples after 3 and 28 days of curing are presented in Table 4.5. Out of all samples cured for 3 days, samples cured at 60 °C (W60 and O) led to the highest total mass loss (16.2-17.6%). This was in line with the strength results, in which samples subjected to elevated temperatures achieved higher strengths than all corresponding samples. Similarly, these were followed by the total mass loss of S and A samples (13.4-14%), whose strength development at early ages followed the same trend. The exothermic peak at ~850 °C observed solely in the DTA curves of W60 and O at 3 days could be attributed to the crystallization to enstatite or forsterite (J. Szczerba et al., 2013). This could be an indication of the higher degree of M-S-H formation under 60 °C used during the curing of W60 and O, as opposed to its formation under 30 °C (Mitsuda & Taguchi, 1977). The difference in the M-S-H structure as well as the extent of the hydration reaction could explain the higher strengths obtained by W60 and O samples at early ages.

A different scenario was observed when the mass loss values of samples cured for 28 days were compared. S samples demonstrated a higher mass loss (19.5%) than all other samples, whereas O samples led to the lowest values (13.8%). A, W30 and W60 samples cured in ambient conditions (A samples) and under water (W30 and W60 samples) revealed similar mass losses ranging between 18.1 and 18.7%. These were in agreement with the strength results, which outlined S and O samples for their highest (50.4 MPa) and lowest (27.7 MPa) 28-day strengths out of all samples, respectively. In line with the trend observed in TGA, A, W30 and W60 samples demonstrated similar 28-day strengths ranging between 35.1 and 41 MPa. The exothermic peak observed at ~850 °C referring to the crystallization process within W60 and O samples at 3 days was observed in all samples at 28 days.

Table 4.5 Mass loss of samples obtained by TGA

Temperature range (°C)	Curing duration (days)	Mass loss (%)				
		Sample				
		S	A	W30	W60	O
40-850	3	14.0	13.4	12.7	17.6	16.2
	28	19.5	18.1	18.7	18.6	13.8
300-450	3	6.2	6.1	6.0	7.0	6.9
	28	7.2	6.9	7.5	6.2	6.3

The progress of hydration within each sample can be assessed via a comparison of their mass losses observed at 3 and 28 days. S, A and W30 samples cured under ambient temperatures revealed an increase in mass

loss, indicating the continuous hydration of MgO and its reaction with MS that led to the formation of M-S-H from 3 to 28 days. This continuous progress of hydration was also reflected in the increase of their strength results from 3 to 28 days. A direct relationship between mass loss observed during TGA and strength development could also be established for W60 samples, which indicated an incremental increase in their mass loss from 3 to 28 days. This could be attributed to the limited formation of M-S-H within these samples between 3 and 28 days, which was supported by their limited strength gain within the same time period. Similarly, a reduction in the mass loss of O samples was observed going from 3 to 28 days. This could indicate a reduction in the amount or a change in the structure of the already established M-S-H due to the loss of its interlayer water when exposed to higher curing temperatures (60 °C). This alteration can explain the corresponding strength loss obtained by O samples at longer durations (> 3 days).

Figure 4.8 shows the relationship between the mass loss associated with M-S-H and compressive strength of all samples at 3 and 28 days. The mass loss values attributed to M-S-H were calculated by subtracting the loss caused by the decomposition of brucite, whose content was determined by XRD-RIR analysis, from the total mass loss. A direct relationship between compressive strength and M-S-H content could be established for all samples, whose strength increased with M-S-H content, regardless of curing duration. This confirmed the critical role of M-S-H on the mechanical performance of MgO-SiO₂ samples. Except for O samples, all samples demonstrated an increase in their M-S-H content as the curing duration increased from 3 to 28 days due to the continuation of the hydration process over time. The trend observed in O samples was consistent with the findings of the earlier analyses, highlighting the contribution of M-S-H formation to strength development.

Figure 4.8 Relationship between the mass loss associated with M-S-H and compressive strength of samples cured for 3 and 28 days

4.2.3.6. FTIR

Figure 4.9 (a) and (b) show the FTIR spectra of all samples cured for 3 and 28 days, respectively. In addition to the samples, the FTIR spectra of the raw materials, MgO and MS, were included for comparison purposes. The characteristic absorption bands due to Si-O stretching (~ 1115 and 803 cm^{-1}) and Si-O-Si bending (475 cm^{-1}) were demonstrated by MS (Perraki & Orfanoudaki, 2008). These were present in all samples, indicating the presence of unreacted silica. The dissolution and reaction of MS to form M-S-H were revealed by the significantly lower intensities of the bands at 803 cm^{-1} due to the Si-O stretching vibration of Q^2 (tetrahedral) observed in all samples in comparison with MS (Nied et al., 2016).

The small band at $\sim 3694\text{ cm}^{-1}$, which was more evident within S, A and O samples at 3 days was ascribed to O-H stretching within $\text{Mg}(\text{OH})_2$. Along with the band at 1650 cm^{-1} , the broad band $\sim 3600\text{-}3300\text{ cm}^{-1}$ present in all spectra referred to O-H vibrations (bending and stretching) (Perraki & Orfanoudaki, 2008; Temuujin, Okada, & MacKenzie, 1998). Similar to their TGA patterns, W60 and O samples reflected similar FTIR spectra at 3 days. Differing from other samples, the Si-O stretching vibration at $\sim 1115\text{ cm}^{-1}$ partially shifted to $\sim 1005\text{ cm}^{-1}$ (Q^3) (Lothenbach et al., 2015; Nied et al., 2016) and formed a broad band within W60 and O samples. An additional broad band centred at $\sim 1115\text{ cm}^{-1}$ resembling its original form in MS was observed in all samples at 3 days. This could be an indication of the higher polymerization within W60 and O samples at early ages, thereby explaining the rapid early strength gain of these samples cured at 60°C .

The 28-day spectra of all samples shown in Figure 4.9 (b) indicated the similar patterns demonstrated by S, A and W30 samples; whereas samples subjected to higher curing temperatures (W60 and O) differed from the rest. The sharp band at 3694 cm^{-1} , indicating the presence of brucite, was observed in all cases. The absorption band due to Si-O stretching vibration at $\sim 1115\text{ cm}^{-1}$ partially shifted to $\sim 1005\text{ cm}^{-1}$ (Q^3) to form a broad band at $\sim 1115\text{-}1005\text{ cm}^{-1}$ within S, A and W30 samples, whereas the Si-O stretching vibrations at $\sim 1115\text{ cm}^{-1}$ appeared as a single shoulder at $\sim 1005\text{ cm}^{-1}$ in W60. In contrast, O samples showed a lower polymerization at 28 days as the absorption band at $\sim 1005\text{ cm}^{-1}$ (Q^3) partially shifted and increased in intensity at $\sim 1115\text{ cm}^{-1}$, forming a shoulder at $\sim 1005\text{ cm}^{-1}$. The Si-O stretching bands at 1115 and 800 cm^{-1} observed within O samples at 28 days resembled the corresponding spectra of MS. This could be an indication of the dissolution of M-S-H after losing its interlayer water. This change in structure could suggest the instability and potential disintegration of M-S-H over time at slightly elevated temperatures.

The formation of the Q^3 Si-O structure at as early as 3 days under elevated curing temperatures could explain the higher strengths of W60 and O samples at early ages, which outperformed the other samples cured under ambient temperatures. A comparison of the 3- and 28-day FTIR spectra revealed the development of the silicate structure from Q^2 (single chains) to Q^3 (sheet-like or interconnected chains), which was more evident within S, A and W30 samples. This change in silicate structure was associated with the strength development of these samples over time. In contrast, despite the early formation of the Q^3 Si-O structure after 3 days of curing, O samples partially transformed to lower polymerization with the reformation of Si-O vibrations at 28 days that resembled MS. This could be indication of the notable strength loss of O samples in the longer durations (> 3 days). These results clearly highlight the significance of the Q^3 Si-O structure on the final phase formations and associated performance implications.

(a)

(b)

Figure 4.9 FTIR spectra of MgO, MS and all samples cured for (a) 3 days and (b) 28 days

4.2.3.7. Microstructure

Figure 4.10 and Figure 4.11 show the FESEM images of all samples cured for 3 and 28 days, respectively. Samples S, A and W30 exhibited similar morphologies of loosely packed gel-like structures of hydration products surrounding spherical SiO_2 particles after 3 days of curing. This was due to slow hydration of MgO and MS at early ages, which resulted in a low degree of loose M-S-H formation at ambient temperatures (30 °C) at 3 days. The formation of hydrate phases initially took place at particle surfaces and gradually expanded inwards, thereby filling up the available pore space. The presence of brucite could also be observed within the microstructures of these samples, indicating the incomplete hydration of MgO as observed earlier in

XRD, TG/DTA and FTIR analyses. S samples revealed a relatively denser structure in comparison to A and W30 samples at 3 days. A similar finding was revealed by W60 and O samples, which demonstrated much denser structures enabled with the formation of hydrate phases, than the other samples at 3 days.

The densification and evolution of the microstructures of S, A and W30 samples were observed after longer curing periods of 28 days. This microstructural development indicated a continuous increase over time associated with the formation of brucite and M-S-H. The similarities between the microstructures of W30 at 28 days and W60 at 3 days hinted the faster rate of microstructural development under elevated temperatures in the presence of water. Unlike S, A and W30 samples, the increase in the curing duration had an opposite effect on the microstructural development of O samples, whose initially dense structure at 3 days was replaced with a much looser arrangement at 28 days. This sample demonstrated the most porous structure out of all samples at 28 days, revealing the effect of high temperature curing on the formation and stability of M-S-H at longer durations. The scarce formation of M-S-H was further supported by the abundant presence of spherical SiO_2 particles in O samples at 28 days. These observations were in agreement with the trends revealed by the XRD, TG/DTA and FTIR results.

(a)

(b)

(c)

(d)

(e)

Figure 4.10 FESEM images of samples cured for 3 days: (a) S, (b) A, (c) W30, (d) W60 and (e) O

(a)

(b)

(c)

(d)

(e)

Figure 4.11 FESEM images of samples cured for 28 days: (a) S, (b) A, (c) W30, (d) W60 and (e) O

4.2.4. Conclusions

This study investigated the strength and microstructural development of reactive MgO-SiO₂ binder systems under different curing conditions. The compressive strength measurements were supported with the microstructural analysis of the microstructure of the samples via XRD-RIR, TG/DTA, FTIR and FESEM analyses. Rapid strength development associated with accelerated dissolution and hydration involving magnesium silicate hydrate (M-S-H) formation was observed at early ages under elevated temperatures (60°C). Although samples cured under ambient temperatures demonstrated a slow rate of M-S-H formation at early ages, their hydration proceeded over time. Samples cured under sealed conditions achieved 28-day strengths >50 MPa because of higher M-S-H contents, higher polymerization and denser microstructures. The content, structure and stability of M-S-H under different conditions determined the overall strength development of MgO-SiO₂ binders.

Chapter 5: DEVELOPMENT OF M-S-H CEMENT WITH RICE HUSK ASH

5.1. Introduction

This study investigated the influence of two different types of RHA (i.e. crystalline and amorphous) as a silica source in MgO-SiO₂ formulations and provided a comparison with corresponding samples containing MS. The overall goal was to assess the potential of RHA to be used as a silica source in the production of M-S-H and evaluate its role in the strength development of MgO-SiO₂ samples. The mechanical performance of the prepared samples was examined via compressive strength development over a duration of 56 days. The reaction mechanisms were observed via isothermal calorimetry and pH measurements. The hydration products and microstructural development were investigated via x-ray diffraction (XRD), thermogravimetric analysis/derivative thermogravimetry (TG/DTG) and Fourier transform infrared spectroscopy (FTIR). These results were further supported with an examination of the morphologies of the final phases via field emission scanning electron microscopy (FESEM).

5.2. Mix details

The details of the mix compositions prepared in this study are presented in Table 5.1. All mixes included 50% MgO and 50% SiO₂ by mass. While the same MgO source was used as the main binder in all mixes, the rest of the mix composition included SiO₂ sources of three different types (MS, RHA-a and RHA-c). Samples M, Rc, Ra and Ra-M contained MS, RHA-c, RHA-a, and RHA-a and MS at equal amounts for their SiO₂ source, respectively. In all 4 samples the water/binder (w/b) ratio was kept constant at 0.55 and 1% (i.e. by mass of solids) SHMP was included as a superplasticizer. The demolded samples were cured in a sealed environment at an ambient temperature of 28±2 °C and RH of 90±5% for up to 56 days until being tested.

Table 5.1 Mix compositions used in this study

Sample	Composition (wt.%)				w/b	SHMP
	MgO	RHA-a	MS	RHA-c		
Ra	50	50	0	0	0.55	1% by
Ra-M	50	25	25	0		weight of
M	50	0	50	0		the total
Rc	50	0	0	50		binder

5.3. Results and Discussion

5.3.1. Characterization of the raw materials

5.3.1.1. PSD

Figure 5.1 shows the PSD of the raw materials MgO, MS, RHA-a and RHA-c. All 4 raw materials demonstrated compatible particle size distributions that partially overlapped. MgO had the smallest particles size amongst all the raw materials, with a d(50) value of 15.0 μm . Amongst the silica sources, RHA-a, which was aimed to substitute MS as a silica source, had a very similar PSD to MS. RHA-a and MS revealed similar d(50) values of 63.3 and 65.9 μm , respectively. The crystalline RHA source, RHA-c, had a slightly smaller PSD compared to RHA-a and MS, with a d(50) value of 28.7 μm .

Figure 5.1 Particle size distribution of MgO, MS, RHA-a and RHA-c

5.3.1.2. XRD

Figure 5.2 shows the XRD diffractograms of the raw materials. MgO displayed high intensity peaks of periclase and minor peaks of magnesite, which was inherited from the parent material due to its incomplete decomposition during the calcination process. Unlike the crystalline peaks observed in MgO, MS revealed a wide hump between 15 and 27° 2θ, which was attributed to an amorphous silica phase. The composition of RHA-c was composed of crystalline peaks of cristobalite, a polymorph of quartz. Differing from RHA-c, RHA-a contained a combination of low intensity crystalline peaks that matched well with the major peaks of cristobalite, as well as an amorphous hump at around 15-27° 2θ, which corresponded to amorphous silica, as seen earlier in MS. Albeit the presence of some crystalline phases, the amorphous nature of RHA-a could present an advantage in the formation of hydrate phases involving silica.

Figure 5.2 XRD patterns of MgO, MS, RHA-a and RHA-c

5.3.1.3. FTIR

Figure 5.3 shows the FTIR spectra of the raw materials. MgO showed main bands at 1424 cm^{-1} and 459 cm^{-1} , which were ascribed to Mg-O bending and stretching vibrations, respectively (Jin & Al-Tabbaa, 2014b; Z. Li et al., 2017). In addition to the sharp band at 3693 cm^{-1} , the small band at 1620 cm^{-1} and the broad band at 3420 cm^{-1} , which were ascribed to OH vibrations (D. Brew & F. Glasser, 2005), indicated the partial hydration of MgO due to the high ambient humidity. Amongst the silica sources, MS and RHA-a exhibited very similar FTIR spectra. Both materials demonstrated a wide band between 1235

and 1000 cm^{-1} and an absorption band at 800 cm^{-1} , which were attributed to Si-O stretching vibrations, as well as an absorption band at 475 cm^{-1} ascribed to O-Si-O bending vibrations (Walling, Kinoshita, Bernal, Collier, & Provis, 2015). Differing from amorphous silica sources, RHA-c revealed an additional absorption band at 622 cm^{-1} attributed to Si-O bending vibrations (D. Brew & F. Glasser, 2005). Furthermore, the band ascribed to Si-O vibrations had a sharp center at 1085 cm^{-1} in RHA-c, as opposed to the broad hump at between $1235\text{-}1000\text{ cm}^{-1}$ observed earlier in MS and RHA-a.

Figure 5.3 FTIR spectra of MgO, MS, RHA-a and RHA-c

5.3.1.4. Microstructure

The microstructural images of the raw materials are shown in Figure 5.4. The microstructure of MgO (Figure 5.4 (a)) consisted of aggregated grains of microparticles, which was consistent with those observed in other studies (Alvarado et al., 2000a; Mo et al., 2010). MS (Figure 5.4 (b)) was composed

of spherical SiO_2 particles with clearly defined boundaries. Alternatively, the morphology and arrangement of particles within RHA-a (Figure 5.4 (c)) resembled those of MgO, in which grains of different sizes were stacked together. Unlike RHA-a, the morphology of RHA-c (Figure 5.4 (d)) was made up of inhomogeneous particles with larger sizes that agglomerated into a dense structure. These variations amongst the microstructures of the silica sources were in line with the differences observed earlier in the XRD patterns and FTIR spectra.

Figure 5.4 FESEM images of (a) MgO, (b) MS, (c) RHA-a and (d) RHA-c

5.3.2. Analysis of samples

5.3.2.1. Isothermal calorimetry

Figure 5.5 shows the heat flow and the cumulative heat associated with the hydration of MgO-SiO₂ pastes measured for up to 72 hours via isothermal calorimetry. As seen in Figure 5.5 (a) and (b), the dissolution of MgO took place a few minutes after mixing for all samples. Variations in the initial hydration peak were recorded depending on the mix composition (i.e. binder component). Ra, Ra-M and M samples, containing amorphous sources of silica, revealed the highest initial heat flow. The lowest initial peak of Rc sample was attributed to the limited reaction of MgO with the crystalline silica. Alternatively, the presence of amorphous silica within Ra, Ra-M and M samples led to peaks with larger intensities, which was an indication of the higher degree of the initial hydration reaction within these samples.

The recorded cumulative heat, shown in Figure 5.5 (c), continued to increase even after 72 hours, indicating the continuation of the hydration process. Out of all samples, M sample revealed the highest cumulative heat throughout the measured period. The higher amount of heat obtained by M sample could be an indication of the higher degree of reaction of Mg²⁺ with MS, in comparison to RHA-a and RHA-c that formed the binder composition within the other samples. Albeit its low initial exothermic peak, Rc sample revealed a similar cumulative heat as Ra and Ra-M samples, which was mainly associated with the hydration of MgO. Although the use of RHA-a in Ra and Ra-M samples led to the highest initial peaks at < 1 hour, this trend did not continue over time. The rapid increase in the initial heat flow of these samples could be an indication of the increased rate of hydration at early ages in the presence of RHA-a, which was not sustained at longer durations.

Figure 5.5 Isothermal calorimetry results of all pastes, showing (a) heat flow during 72 hours, (b) heat flow during the first 1 hour and (c) cumulative heat released during 72 hours

5.3.2.2. pH

Figure 5.6 (a) and (b) show the pH values of the raw materials and the samples over 28 days of curing, respectively. The initial pH values of the raw materials, as seen in Figure 6 (a), ranged between 9.5-11.4. MgO had the highest pH values amongst all, which demonstrated an increase in the initial pH to around 11.6 due to the release of OH^- ions. This was followed by a decrease and the stabilization of pH at a range of 11.0-11.2 at 28 days. A similar trend was observed in RHA-a and RHA-c, whose similar pH values were levelled at around 9.6 and 10.1 after a few days of measurement, respectively. Differing from the RHA sources, the pH of MS continued to decrease even after 7 days, reaching below 8.0 at 28 days. The continuous reduction in the pH of MS was attributed to the dissolution of silica, which continued for a longer duration than those of RHA-a and RHA-c, whose pH stabilized in shorter period.

The pH values of MgO-SiO_2 samples during the first 28 days of curing are shown in Figure 5.6 (b). The initial increase observed in the pH of all samples was associated with the dissolution of MgO, which resulted in the release of OH^- ions. A decrease in the pH of Ra, Ra-M and M samples was recorded after 1 day, which could be due to the dissolution of SiO_2 and subsequent formation of M-S-H. Among these 3 samples, Ra and M samples revealed the highest and lowest pH values throughout the entire measurement period, respectively. Ra-M sample, whose silica source was composed of an equal combination of RHA-a and MS, demonstrated intermediate pH values (i.e. pH of $\text{Ra} > \text{Ra-M} > \text{M}$), which was an indication of the role of silica in determining the final pH. The lowest pH values of M samples, whose reduction could be an indication of the extent of hydration, were in line with the trend observed in the pH of the raw materials (Figure 5.6 (a)), where MS revealed the lowest pH amongst all silica sources. Unlike the other samples, the use of RHA-c in Rc sample led to pH values similar to the pH of MgO due to the lack of reaction between Mg-phases and silica.

(a)

(b)

Figure 5.6 pH values of (a) raw materials and (b) all samples during the first 28 days of curing

5.3.3. Compressive strength

Figure 5.7 shows the compressive strength of all samples cured for up to 56 days. Ra sample, which contained RHA-a as its silica source, exhibited rapid strength gain and highest early strengths that reached 22 and 35 MPa at 3 and 7 days, respectively. This fast strength development of Ra sample could be attributed to a combination of physical and chemical effects. In terms of its physical contribution, RHA-a could act as a filler, thereby contributing to strength development via the formation of a dense structure. Furthermore, the reaction between the amorphous SiO_2 in RHA-a and MgO could lead to the formation of M-S-H, which is known to provide strength in MgO- SiO_2 formulations (Sonat, Dung, & Unluer, 2017; T. Zhang et al., 2014b). The compressive strength of Ra sample remained relatively stable at around 33 MPa at 28 days, while a reduction was observed in the longer durations, resulting in a strength of 26 MPa at 56 days. This unexpected reduction could be associated with the volume instability of Ra sample due to the formation of hydrate phases in the later ages. At early ages (≤ 7 days) the rapid formation of M-S-H may have covered the surface of unreacted MgO particles, resulting in a reduced amount of surface area available for further hydration and hindering access to unhydrated zones (Mo et al., 2010). At longer curing durations (≥ 28 days) with the penetration of pore water towards the unhydrated MgO surfaces, further hydration might have taken place, resulting in the initiation of cracks due to the expansive nature of brucite formation.

Figure 5.7 Compressive strengths of all samples cured for up to 56 days

Alternatively, M sample, which consisted of MS as its silica source, exhibited a consistent strength development over 56 days. Although the rate of strength development reduced gradually, a continuous increase in strength was observed throughout the 56 days of curing. This strength gain demonstrated by M sample was an indication of the continuous formation of hydration products even in the longer periods. The continuation of the hydration reaction within the M sample led to the highest strengths amongst all samples at 56 days (47.5 MPa), which was 64% and 84% higher than the corresponding strengths of Ra-M and Ra samples, respectively.

Ra-M sample, which consisted of a combination of RHA-a and MS at equal amounts as its silica source, exhibited a similar compressive strength development to M sample during the first 7 days of curing. Although the strength development of Ra-M sample continued after 7 days, it revealed lower strengths than M sample and equivalent strengths to the Ra sample as the duration of curing increased beyond 7 days. This relatively lower strength of Ra-M sample could be attributed to its lower MS content when compared to M sample.

When the silica source was set as RHA-c within Rc sample, an obvious reduction in strength was observed. Accordingly, Rc sample revealed the lowest strengths among all samples throughout 56 days. While these samples were too weak for strength testing at 3 days, they could only reach 3 and 12.5 MPa at 7 and 56 days, respectively. This limited strength development was associated with the inability of crystalline silica to react with Mg-phases and result in the formation of any strength providing hydration products. Therefore, any strength, albeit low, was provided by the formation of brucite, which is known to offer limited strength in MgO systems (M. Liska, L. J. Vandeperre, & A. Al-Tabbaa, 2008). These variations in the strength results amongst different samples highlight the role of reactive forms of silica in the strength development of MgO samples.

Overall, the compressive strength results showed that Ra sample, containing RHA-a, revealed the highest strengths at early ages (≤ 7 days); whereas M sample, containing MS, demonstrated a continuous strength gain and led to the best performance amongst all samples in the longer durations (> 7 days). Ra-M sample exhibited a moderate strength gain, resulting in lower early age (≤ 7 days) strengths than Ra sample and lower strengths than M sample in the longer durations. Although the 56-day strengths of Ra-M could not reach those of M sample, a constant increase in strength was observed throughout the 56 days, unlike Ra sample, which was associated with the partial presence of MS within Ra-M sample.

The strength development was mainly due to the formation of hydrate phases, namely M-S-H, via the reaction of silica with Mg-phases during the curing process. MS continued to react with MgO and form hydration products in the longer durations, whereas the extent of the reaction between RHA-a and MgO was limited to early ages. These findings were in line with the pH measurements shown in Figure 5.6 (a), where the pH of MS solution continued to decrease even after 7 days, while the pH of RHA-a solution

stabilized after a few days. This lack of change in the pH was an indication of the limited dissolution of SiO_2 within the RHA-a solution in the longer periods. A similar outcome was seen in the pH values of the extracted samples shown in Figure 5.6 (b), where M sample revealed a continuous decrease and the lowest pH results amongst all samples. Despite the comparatively lower strengths of samples containing RHA-a than those with MS, the high early strength gain and the satisfactory long term strengths of the former indicate the potential of RHA-a to be utilized as partial replacement for MS in MgO-SiO_2 systems.

5.3.4. XRD

Figure 5.8 shows the XRD diffractograms of all samples cured for 7 and 56 days. Some of the main phases observed were MgO (at 36.9° , 42.9° , 62.3° , 74.7° and 78.6° 2θ) and brucite (at 18.6° , 38.0° , 50.8° , 58.6° and 68.2° 2θ), in addition to fluorite (at 28.3° , 47.0° and 55.8° 2θ), which was used as a reference. Within samples containing amorphous silica (Ra, Ra-M and M), broad peaks indicative of amorphous M-S-H (at $17-28^\circ$, $32-39^\circ$ and $58-62^\circ$ 2θ) were identified. While the amorphous silica peak within these silica sources, located at around $15-27^\circ$ 2θ as shown earlier in Figure 5.2, largely disappeared in all mixes, the presence of MgO even after 56 days of curing was an indication of its incomplete dissolution and lack of hydration.

Amongst the samples cured for 7 days (Figure 5.8 (a)), the presence of amorphous M-S-H peaks (especially at $58-62^\circ$ 2θ) were more obvious within Ra and Ra-M samples, which could indicate that RHA-a contributed to M-S-H formation more rapidly compared to MS at early ages. Similarly, while the presence of brucite was very minimal within Ra and Ra-M samples, M sample revealed the presence of brucite. The formation of M-S-H and lack of brucite within samples containing RHA-a could be an indication of the rapid reaction

of Mg-phases with the silica source, forming M-S-H at early ages. Alternatively, in addition to brucite, the presence of the amorphous silica peak at around $22^\circ 2\theta$ within M sample suggested the incomplete dissolution of silica at 7 days. These observations were in line with the pH of the raw materials (Figure 5.6 (a)), where the pH of MS solution continued to decrease, as opposed to the stable pH values revealed by the RHA-a solution after 7 days. Rc sample revealed high intensity cristobalite peaks, which originated from the raw material RHA-c, in addition to the MgO and brucite peaks. Differing from the other 3 samples, Rc did not reveal an observable M-S-H peak, which was due to the lack of the dissolution of its silica source and the absence of any reaction between silica and Mg-phases. The formation of brucite as the main hydrate phase within this sample could explain its limited early strengths.

(a)

(b)

Figure 5.8 XRD diffractograms of all samples (a) at 7 days and (b) 56 days

The XRD diffractograms of all samples cured for 56 days (Figure 5.8 (b)) revealed the presence of MgO and brucite, indicating incomplete hydration even after 56 days of curing. Similar to the observations at 7 days, the presence of M-S-H was seen within Ra and Ra-M samples at 56 days without a significant change in the amorphous humps, whereas M sample revealed an obvious increase in the intensity of its M-S-H peaks from 7 to 56 days. The intensity of the brucite peak reduced with an increase in the amount of RHA-a content, almost disappearing in the Ra sample, whose silica source was only RHA-a. This observation suggested that the type and properties of the silica source played a role in the extent of the hydration reaction, and hence the utilization of brucite. Rc sample revealed the highest brucite peak amongst all samples. When coupled with the cristobalite peaks, whose intensity did not show any major decrease over time, the presence of brucite suggest that RHA-c did not react with Mg-phases to form M-S-H even after 56 days.

The amounts of MgO and Mg(OH)₂ present in all samples at 7 and 56 days, as quantified by XRD-RIR, are listed in Table 5.2. At 7 days, samples that incorporated amorphous silica sources (Ra, Ra-M and M) revealed similar MgO contents (~25%). Samples Ra and Ra-M, which included the use of RHA-a, contained ~3% brucite, whereas this value was higher at ~8% for M sample at 7 days. The lowest content of brucite within Ra could be an indication of its increased conversion to M-S-H. Alternatively, the high MgO content of Rc sample was an indication of the lack of hydration and thereby the formation of any strength providing hydrate phases within this sample.

Table 5.2 MgO and Mg(OH)₂ contents obtained by XRD after 7 and 56 days of curing

Sample	Content (%)			
	7 days		56 days	
	MgO	Mg(OH) ₂	MgO	Mg(OH) ₂
Ra	25.6	2.7	17.4	4.7
Ra-M	24.8	3.0	10.2	5.9
M	25.4	8.2	10.8	7.3
Rc	37.6	6.3	28.3	15.2

When the phase contents obtained at 56 days were compared, the lowest MgO contents (~10%) were revealed by Ra and M samples, which was due to the continuation of the hydration reaction and thereby the utilization of MgO in the longer term. Differing from these samples, Ra sample contained a higher MgO content of ~17%. This relatively higher MgO content of Ra sample could suggest that the rapid formation of hydration products at early ages may have

hindered the continuation of the hydration reaction by forming a layer on the surface of unreacted particles. While the brucite contents of all other samples increased over time from 7 to 56 days, a decrease was observed in M sample. This could be an indication of the utilization of brucite in the formation of M-S-H, which was supported by the obvious increase in the amount of M-S-H observed in the XRD patterns and the increase in the compressive strength of M sample from 7 to 56 days. Alternatively, the increase in the brucite content of Rc sample and its higher MgO content in comparison to other samples was an indication of the lack of reaction between the crystalline silica and Mg-phases and thereby the inadequate strength development, which only relied on the limited formation of brucite as opposed to M-S-H.

5.3.5. TG/DTG

Figure 5.9 and Figure 5.10 show the TG/DTG plots of all samples cured for 7 and 56 days, respectively. When the total mass losses revealed by all samples were compared, Rc sample revealed the lowest mass loss amongst all samples at both curing durations. This difference was more significant at 7 days, after which Rc sample exhibited a notable formation of brucite and revealed closer mass loss values to the rest of the samples at 56 days. The lower mass loss of Rc sample than other samples were in line with its inferior mechanical performance and was attributed to the inert nature of the crystalline silica source, which did not contribute to the hydration reaction.

Alternatively, samples with amorphous silica sources (Ra, Ra-M and M) revealed similar total mass loss values at both curing durations. Although the total mass loss values of these samples were similar, the type and content of the formed hydrated phases exhibited some differences, as inferred from the varying intensities of DTG peaks shown in Figure 5.9 (b) and Figure 5.10 (b). Amongst these 3 samples, those that demonstrated the highest compressive strengths (i.e. Ra sample at 7 days and M sample at 56 days) exhibited slightly lower total mass loss values at both curing durations. This observation

suggested that mechanical performance was not only correlated to the total mass loss, but was determined by the type of hydrate phases (M-S-H vs. brucite) that formed. In MgO-SiO₂-H₂O systems, the main steps involved during thermal decomposition can be summarized as below (Lothenbach et al., 2015; Nied et al., 2016):

1. 30-300 °C: Loss of interlayer water of M-S-H
2. 300-750 °C: Decomposition of brucite and separation of hydroxyl groups in M-S-H
3. 750-900 °C: Dehydroxylation of silanol groups

In addition to these decomposition reactions, additional mass loss associated with adsorbed water could be seen in the 30-300 °C temperature range. Although all samples were dried before TGA, it is common to observe some mass loss below 150 °C due to the dehydration of physically attached water. Furthermore, the decomposition of undecomposed magnesite within MgO, whose presence was shown earlier in Figure 5.2, also contributed to the total mass loss within the 300-750 °C range, as observed from the 2 small peaks at ~550 °C and ~650 °C on the DTG plots (Figure 5.9 (b) and Figure 5.10 (b)). Finally, the loss on ignition (LOI) associated with impurities (i.e. undecomposed phases) within the raw materials, was also considered in the total mass loss of each sample. Accordingly, the LOI of MgO, MS, RHA-a and RHA-c were measured as 6.3%, 2.2%, 5.2% and 1.3% respectively. These decomposition temperatures and corresponding mass loss values revealed by the TG/DTG analysis were used to quantify the hydrate phases within each sample, whose details are provided in the following section.

(a)

(b)

Figure 5.9 Thermogravimetric analysis results of all samples at 7 days, showing the (a) TG and (b) DTG plots

(a)

(b)

Figure 5.10 Thermogravimetric analysis results of all samples at 56 days, showing the (a) TG and (b) DTG plots

5.3.6. Phase quantifications from DTG

Figure 5.11 and Figure 5.12 show the deconvoluted DTG curves for all samples cured for 7 and 56 days, respectively. The plots included the original data (represented by the black dots) as well as the cumulative fit (represented by the solid lines) for each sample. In addition to these two sets, the deconvoluted curves, whose combination formed the cumulative fit, were presented. Each sample consisted of a series of deconvolution curves, which represented different decomposition reactions. For instance, two curves were used to represent the dehydration of adsorbed water and loss of internal layer of M-S-H below 300 °C within Ra, Ra-M and M samples. A peak centered at ~400 °C, was used to represent the dehydroxylation of brucite in all samples. To represent the LOI of the raw materials (MgO and SiO₂ sources) and the dehydroxylation of M-S-H, a combination of two wide curves were used. For Rc sample at 56 days (Figure 5.12 (d)), 3 curves represented the dehydration of adsorbed water, dehydroxylation of brucite and LOI of raw materials, as M-S-H did not form within this sample. One additional curve, which is attributed to decomposition of magnesite within MgO, was used for Rc sample at 7 days to obtain a better.

Figure 5.11 Deconvoluted DTG curves of (a) Ra, (b) Ra-M, (c) M and (d) Rc samples at 7 days

Figure 5.12 Deconvoluted DTG curves of (a) Ra, (b) Ra-M, (c) M and (d) Rc samples at 56 days

Table 5.3 shows the mass loss values based on the deconvoluted DTG curves for all samples cured for 7 and 56 days. Rc sample revealed the lowest mass loss values due to dehydration than the rest of the samples at both curing durations, which could be attributed to the lack of M-S-H formation in the presence of crystalline silica. Other samples containing amorphous silica (Ra, Ra-M and M) demonstrated higher mass loss values within this initial temperature range, which also included the mass loss due to the loss of interlayer water from M-S-H. The mass loss due to brucite dehydroxylation was the lowest for Ra sample at 7 days, which was in line with the XRD observations. Alternatively, Rc sample demonstrated the highest mass loss from brucite dehydroxylation at 56 days (5.6% vs. 2.2-2.5% of other samples),

which could be attributed to the lack of reaction between brucite and crystalline silica, as was also shown earlier in XRD and strength results. Similar to the phase quantifications obtained via XRD-RIR (Table 5.2), the mass loss associated with brucite increased from 7 to 56 days for all samples except for M sample, whose reduced brucite content could indicate the formation of M-S-H over time.

The last two columns in Table 5.3 show the mass loss due to the dehydroxylation of M-S-H within all samples at 7 and 56 days. These values also involved the mass loss from the LOI of the raw materials. This was obvious from the mass loss values of Rc sample, for which LOI was the main contributor to mass loss within this range as M-S-H formation was not observed in the presence of crystalline silica. Amongst the other 3 samples, the highest increase in the mass loss associated with M-S-H dehydroxylation from 7 to 56 days was revealed by M sample. This increase could refer to the continuous formation of M-S-H within M sample, which was consistent with the XRD patterns and the higher strength results of this sample as the curing duration increased.

Table 5.3 Mass loss values based on the deconvoluted DTG curves for all samples cured for 7 and 56 days

Sample	Mass loss (% of original weight)					
	Dehydration		Brucite		M-S-H	
	of adsorbed water		dehydroxylation		Dehydroxylation	
	7 days	56 days	7 days	56 days	7 days	56 days
Ra	6.6	6.7	1.2	2.5	12.6	13.9
Ra-M	7.7	7.9	1.8	2.2	12.1	13.5
M	8.2	5.5	2.7	2.2	10.0	13.2
Rc	2.1	3.0	2.7	5.6	7.4	9.9

Figure 5.13 shows the correlation of compressive strength vs. brucite dehydroxylation and M-S-H dehydroxylation for Ra, Ra-M, and M samples. For this figure the Ra samples was not included as it is known that M-S-H was not formed within Ra sample. It is observed that there is overall a proportional relationship between compressive strength and M-S-H dehydroxylation; while the data for compressive strength vs. brucite dihydroxylation was rather scattered. This shows the significance of M-S-H formation on compressive strength.

Figure 5.13 Correlation of compressive strength vs. (a) brucite dehydroxylation and (b) M-S-H dehydroxylation for Ra, Ra-M, and M samples

5.3.7. FTIR

Figure 5.14 (a) and (b) show the FTIR spectra of all samples cured for 7 and 56 days, respectively. At 7 days, all samples exhibited structural OH^- bond bands at ~ 1640 and $\sim 3400 \text{ cm}^{-1}$ (Jin & Al-Tabbaa, 2014b), which had higher intensities than those of the raw materials (Figure 5.3). This could indicate the

formation of new OH⁻ bonds, which could explain the strength development at 7 days. The Mg-OH stretching band at 3693 cm⁻¹ (D. Brew & F. Glasser, 2005), indicating the presence of brucite, was more pronounced in Rc sample in comparison to others at 7 days. The band at ~1430 cm⁻¹, which could be ascribed to Mg-O bending vibration, was present in all samples at 7 days. This band was associated with unreacted MgO, in line with the XRD observations. The absorption bands at ~800 and ~475 cm⁻¹, which were also observed in the silica sources/raw materials (MS, RHA-a and RHA-c), were present in all samples, albeit at lower intensities than the raw materials. This suggested that silica was not fully consumed in any of the samples at 7 days. All samples exhibited bands that were ascribed to Si-O bands between the wide range of ~980-1120 cm⁻¹ with slight shifts amongst the samples. These bands could refer to the silica sources or the newly formed Si-O chains in M-S-H. Within the 980-1120 cm⁻¹ range, two shoulders were observed in all samples except for Ra-M sample, in which three shoulders were observed. The additional shoulder could be due to the two different silica sources (RHA-a and MS) included in Ra-M sample. A small peak at ~890 cm⁻¹ attributed to the Si-OH group of layered M-S-H (Jin & Al-Tabbaa, 2014b; Z. Li et al., 2017), which was not present in any of the raw materials, appeared in all samples, indicating the formation of a new phase.

(a)

(b)

Figure 5.14 FTIR spectra of all samples at (a) 7 days and (b) 56 days

The FTIR spectra of all samples at 56 days (Figure 5.14 (b)) exhibited similar bands as those observed at 7 days, with some minor changes. The intensities of the OH⁻ bonds at ~1640 and ~3400 cm⁻¹ increased for all samples when compared to 7 days, indicating the continuation of hydration from 7 to 56 days. The intensity of the band at 3693 cm⁻¹ was higher for Rc sample than all other samples at 56 days. This was an indication of the higher brucite content within Rc sample in comparison to other samples at 56 days, which was in line with the XRD and TG/DTG observations. The absorption band at ~800 cm⁻¹, attributed to Si-O stretching vibrations in the silica sources, diminished for M sample. These changes were an indication of the utilization of MS within M sample after 56 days of curing. This absorption band (~800 cm⁻¹) could still be observed in Ra sample, whereas it had a prominent presence in Rc sample, indicating that silica sources were not fully utilized in those samples even after 56 days. The existence of the adsorption band at ~800 cm⁻¹, which was fully diminished in M sample, within Ra sample, indicated that MS dissolved at a higher extent in comparison to RHA-a at longer durations. The lack of any significant change in the intensity of the same absorption band (~800 cm⁻¹) between 7 and 56 days in Ra sample was in line with the stability of the pH of the RHA-a suspension after 7 days. Ra, Ra-M and M samples demonstrated similar patterns within the ~980 to 1120 cm⁻¹ range that was ascribed to Si-O stretching vibrations, which suggested that RHA-a and MS resulted in final hydrate phases (M-S-H) with similar structures.

5.3.8. Microstructure

Figure 5.15 shows the FESEM images of all samples after 7 days of curing. Ra sample (Figure 5.15 (a)) demonstrated a more homogenous microstructure composed of particles that were more densely packed together when compared to other samples, which could explain its high early strengths. In Ra-M sample (Figure 5.15 (b)), the partial formation of hydration products could be seen surrounding other particles, in addition to the SiO₂ spheres that resembled the microstructures of both MS and RHA-a. The presence of loose,

unreacted spherical SiO_2 particles was more clearly observed for M sample (Figure 5.15 (c)) in comparison to Ra-M sample. In addition to unreacted spherical SiO_2 particles, a cloudy, gel-like structure, which could be attributed to the partial formation of M-S-H was observed. The existence of SiO_2 particles within Ra-M and M samples was an indication of the incomplete utilization of silica. In addition to unreacted SiO_2 particles, the less abundant formation of hydration products was the main reason for the lower compressive strengths of these samples when compared to Ra sample at 7 days. Unlike Ra-M and M, Ra sample showed the well-distributed formation of M-S-H gel, whereas the presence of unreacted SiO_2 particles was less abundant. Alternatively, Rc sample (Figure 5.15 (d)) did not indicate the formation of any gel-like hydration products, but instead exhibited some brucite and unreacted MgO particles, which were loosely arranged into clusters with rough and inhomogeneous surfaces. These findings were in line with the XRD and TGA results, also explaining the variations in the mechanical performance of each sample according to the density of their microstructures and the presence of hydrate phases.

(a)

(b)

Figure 5.15 FESEM images of (a) Ra, (b) Ra-M, (c) M and (d) Rc samples at 7 days

Figure 5.16 shows the FESEM images of all samples after 56 days of curing. Ra sample (Figure 5.16 (a)) exhibited a microstructure consisting of different sized and shaped particles stacked together. Differing from well-packed and dense microstructure it had demonstrated at 7 days, Ra sample revealed a loosely packed structure at 56 days. This change over time could explain the reduction in the strength of Ra sample from 7 days to 56 days. Alternatively, M sample (Figure 5.16 (c)) exhibited a dense structure composed of a well-connected network without many loose particles of unreacted brucite/MgO. This network was mainly established via the dense and formation of M-S-H throughout the structure, which could explain the continuous strength development of M sample until 56 days. Unreacted spherical SiO_2 particles were much less abundant compared to the microstructures observed at 7 days, indicating that the formation of M-S-H proceeded over time. The continuous formation of M-S-H gel corresponded well with highest strengths obtained by M sample, which outperformed the rest of the samples at 56 days. Ra-M sample resembled the microstructures of both Ra and M samples at different locations, revealing a continuous layer on the left hand-side and a

rough morphology consisting of loosely packed small particles on the right hand-side of Figure 5.16 (b). The partial formation of M-S-H gel was accompanied with a cluster of unhydrated particles as well as brucite within Ra-M sample, which indicated that different SiO_2 sources may have led to the formation of different hydrate phases. The increase in the compressive strength of Ra-M sample from 7 to 56 days could be attributed to the partial formation of M-S-H observed in its microstructure. Rc sample (Figure 5.16 (d)) presented the formation of brucite along with unreacted MgO and silica particles, resulting in a rough and discontinuous microstructure. The absence of a well-connected network enabled via the formation of M-S-H was the main reason for the lower strengths of Rc sample even after 56 days of curing.

Figure 5.16 FESEM images of (a) Ra, (b) Ra-M, (c) M and (d) Rc samples at 56 days

5.4. Conclusions

Rice husk ash (RHA) is a waste material obtained from the combustion of rice hulls. The properties of RHA, such as its crystallinity and reactivity, depend on the combustion conditions. This study investigated the use of RHA as a silica source in MgO-SiO_2 based samples. Two different RHA sources (i.e. crystalline and amorphous) were used in comparison to microsilica (MS), which is commonly used in MgO-SiO_2 formulations to form magnesium silica hydrate (M-S-H). Isothermal calorimetry and pH measurements were used to analyze the hydration process. In addition to compressive strength measurements, microstructural analysis was performed via XRD, TG/DTG, FTIR and FESEM. Samples containing amorphous RHA as the silica source achieved the highest compressive strengths at early ages (34 MPa at 7 days), whereas those containing MS revealed the highest strengths in the long term (47 MPa at 56 days). Formation of M-S-H was clearly observed in all samples containing amorphous RHA or MS. The use of crystalline RHA led to low strengths due to the absence of M-S-H formation. Amorphous RHA has the potential to partially or fully replace microsilica in MgO-SiO_2 formulations, which also presents environmental and economical benefits.

Chapter 6: INFLUENCE OF CARBONATION CURING ON MgO AND MgO-SiO₂ BASED SAMPLES

6.1. Introduction

This study aims to investigate the properties of binders involving the combination of MgO-SiO₂-H₂O and carbonated MgO systems and their capacity to increase the utilization of MgO and Mg(OH)₂ via the formation of an extensive network composed of Mg-carbonates and M-S-H. The influence of carbonation on the MgO-SiO₂-H₂O system was evaluated via a detailed comparison of MgO-SiO₂ and MgO-based concrete samples with the same binder content. The prepared samples were subjected to sealed and carbonation conditions to assess their performance with and without the introduction of CO₂ curing. The mechanical performance of the MgO-SiO₂ (MS) and MgO (M) systems was studied with compressive strength testing at different durations up to 56 days. The strength results of each system were supported with an analysis of their microstructural development along different stages of curing. The formation of hydrate and carbonate phases were investigated via X-ray diffraction (XRD) and thermogravimetric/derivative thermogravimetric analysis (TG/DTG), while the microstructural development of the prepared formulations was observed by field emission scanning electron microscopy (FESEM).

6.2. Mix details and curing conditions

Table 6.1 shows the mix compositions prepared under this study and the corresponding curing conditions each mix was subjected to. Two different binder systems composed of MgO (M samples) and MgO-SiO₂ (MS samples), in which MgO and microsilica were introduced at a ratio of 1:1, were prepared. These binders were used in the preparation of concrete samples that were composed of 40% binder (i.e. to provide binding in the absence of fine

aggregates, which were omitted from the mix design to avoid contamination with quartz and provide an accurate quantification of hydrate and carbonate phases during microstructural analysis) and 60% coarse aggregates, by mass. All formulations were prepared with a constant water/binder (w/b) ratio of 0.45 and included 1% (i.e. of the total binder content) of SHMP to improve fluidity, which led to fully compacted samples for both systems. The prepared samples were subjected to two different curing conditions: (i) Sealed (S) under 95% relative humidity (RH), ambient temperature and ambient CO₂ concentration; and (ii) carbonated (C) under 95% RH, ambient temperature and 10% CO₂ concentration.

Table 6.1 Mix compositions and corresponding curing conditions.

Sample	Composition (wt.%)			Curing condition
	MgO	Microsilica	Coarse aggregates	
M-S	40	0	60	Sealed
M-C	40	0	60	Carbonated
MS-S	20	20	60	Sealed
MS-C	20	20	60	Carbonated

6.3. Results and Discussion

6.3.1. Density

The wet density values of all samples over the 56 days of curing are shown in Figure 6.1. The initial densities of M samples before the start of the curing process were ~8% higher than those of MS samples (2.33 vs. 2.16 g/cm³). This was associated with the differences in the compositions of the binder components of each system. For both systems, samples cured under sealed conditions (M-S and MS-S) revealed relatively constant densities throughout the curing process. Any increase in density due to the progress of the hydration reaction that resulted in the expansive formation of hydrate phases within these samples could have been partially overshadowed with the loss of unbound water from the pore system during curing. Alternatively, the introduction of carbonation led to a noticeable increase in the densities of both systems. The densification process was more visible within M-C samples, which demonstrated ~5% increase in their densities over 56 days, revealing a final density of 2.44 g/cm³. Corresponding MS-C samples revealed an increase of ~1.5% over 56 days. The final density of MS-C samples was recorded as 2.19 g/cm³, which was lower than that of M samples, similar to the trend observed before curing initiated. Apart from the initial and final densities, the change in the sample density over time during the curing process could be an indication of the performance of each formulation under different curing conditions.

Figure 6.1 Density of all samples during 56 days of curing

6.3.2. Compressive strength

Compressive strengths of samples cured for up to 56 days are shown in Figure 6.2. Carbonated MgO (M-C) samples achieved the highest strengths amongst all samples throughout the entire curing duration. The corresponding MgO samples that were subjected to sealed conditions (M-S) revealed the lowest strengths of around 18 MPa, which remained relatively stable throughout 56 days due to the low ambient CO₂ concentrations that slowed down the carbonation process. Alternatively, the rapid strength gain exhibited by M-C samples was associated with the elevation of the CO₂ concentration to 10% during the curing process, which was in line with the findings of previous studies (Dung & Unluer, 2017a; M Liska et al., 2008). The presence of CO₂ enabled the carbonation reaction within M-C samples, which reached early-age strengths as high as 56 and 77 MPa at 3 and 7 days, respectively. The difference in the CO₂ concentration used in the curing of M-S and M-C

samples led to an up to ~330% difference in their performance. This significant transformation in strength is a clear indication of the critical role that carbonation plays in the mechanical performance of MgO-based formulations, whose strength gain dominantly relies on the formation of carbonate phases, as reported in the literature (Martin Liska & Abir Al-Tabbaa, 2009; M Liska et al., 2008; C. Unluer & Al-Tabbaa, 2014; L. J. Vandeperre & Al-Tabbaa, 2007). This increase in strength within the carbonated samples was in line with the increase in the density of samples reported earlier in Figure 6.1, where M-C samples revealed a noticeable increase in their density due to the formation of carbonates.

Figure 6.2 Compressive strength of all samples subjected to 56 days of curing

Samples, whose binder component consisted of MgO-SiO₂ (MS-S and MS-C), demonstrated a consistent strength development over 56 days. The use of carbonation curing in MS-C samples enabled 56-day strengths as high as 73 MPa, while the corresponding MS-S samples cured under sealed conditions revealed a strength of 56 MPa. The difference in strength was more pronounced at early ages (3 days), during which MS-C samples achieved up to ~60% higher strengths than MS-S samples. This difference gradually reduced and stabilized at ~20% for the remaining curing durations. The high difference at earlier ages was mainly due to the different curing conditions these two sets of samples were subjected to. While the formation of M-S-H was the main source of strength in MS-S samples, the higher strengths obtained by MS-C samples were attributed to the formation of carbonate phases. As the carbonation process takes place more rapidly at early stages of curing and gradually slows down with the densification of the microstructure, the trends observed in the strength difference of MS-S and MS-C samples were in line with the expected progress of carbonation.

Amongst the four sets of samples prepared under this study, those subjected to carbonation curing (M-C and MS-C) demonstrated the best performance for each binder composition (MgO and MgO-SiO₂). Although the highest strengths were achieved by M-C samples at early ages (≤ 7 days), the consistent strength development of MS-C samples led to similar results at longer durations (≥ 28 days). In addition to the binding strength associated with the carbonate network that formed during the curing process, the higher densities revealed by M-C samples in comparison to MS-C samples may have contributed to their strength development. Alternatively, while the formation of M-S-H within MS-S samples resulted in a considerable performance without carbonation, the incorporation of carbonation in the curing process significantly enhanced the strength development of these samples. However, when compared to MgO-SiO₂ (MS) samples, which also gained strength via the hydration process that led to the formation of M-S-H; the progress of carbonation was much more critical for purely MgO-based (M)

samples, whose strength development mainly depended on the conversion of Mg-phases (MgO and $\text{Mg}(\text{OH})_2$) into carbonates.

6.3.3. Microstructure

Figure 6.3 shows the FESEM images of all samples after 3 days of curing. M-S sample (Figure 6.3 (a)) indicated a loose formation of brucite around MgO particles, whereas an extensive formation of various HMCs, namely needle-like nesquehonite and rosette-like hydromagnesite/dypingite, were observed in the M-C sample (Figure 6.3 (b)). The dense formation of these HMCs could explain the high strength gain (56 MPa) achieved by M-C samples at as early as 3 days. Similar to M-S, MS-S sample (Figure 6.3 (c)) mainly displayed the formation of brucite (i.e. lamellar aggregates of platelets (Y. Gao, Wang, Su, Shen, & Wang, 2008)) along with M-S-H (i.e. continuous layer covering other particles (Chen, Li, Li, Chou, & Hou, 2016; Z. Li et al., 2017)), which slightly led to the densification of the microstructure. The resemblance in the microstructures of M-S and MS-S samples corresponded well with their identical 3-day strengths. The use of carbonation curing in MS-C sample (Figure 6.3 (d)) clearly revealed the formation of rosette-like hydromagnesite/dypingite with large flakes, along with M-S-H, which could explain the higher strengths obtained by this sample in comparison to MS-S. The morphology of hydromagnesite/dypingite observed within MS-C sample differed from those seen in M-C, where the agglomeration of smaller crystals produced a denser microstructure. Coupled with the dense formation of nesquehonite needles, the densification of the sample microstructure can explain the carbonation-related rapid strength gain of M-C at 3 days.

Figure 6.3 FESEM images of (a) M-S, (b) M-C, (c) MS-S and (d) MS-C samples at 3 days

Figure 6.4 shows the FESEM images of all samples after 28 days of curing. Although it was cured for a longer duration, M-S sample (Figure 6.4 (a)) mainly indicated the formation of brucite along with unreacted MgO. The limited formation of carbonates was as expected since the ambient concentration of CO_2 used during the curing of M-S samples was not sufficient for a noticeable formation of carbonates, thereby limiting strength development. Differing from M-S, M-C sample (Figure 6.4 (b)) revealed the dense formation of interlocked nesquehonite and artinite, along with hydromagnesite/dypingite. The simultaneous formation of various carbonate

phases corresponded well with the highest strengths obtained by M-C samples, which outperformed all others during the entire curing period. Formation of a continuous gel-like M-S-H layer, similar to those reported in earlier studies (Chen et al., 2016; Z. Li et al., 2017), was observed in the microstructure of MS-S sample (Figure 6.4 (c)), which could explain its steady strength development with time. The spherical SiO_2 particles were less abundant when compared to the microstructure of MS-S sample cured for 3 days. The reduction in the amount of SiO_2 was in line with the increase in M-S-H formation as silica was consumed in the hydration reaction over time. When subjected to carbonation, MS-C sample (Figure 6.4 (d)) exhibited the presence of a dense nesquehonite cluster, which formed a wall-like structure via the combination of individual needles. Along with nesquehonite, rosette-like hydromagnesite/dypingite agglomerates contributed to the densification of the microstructure. Amongst the HMCs, the loose presence of spherical SiO_2 particles was observed, whereas the gel-like M-S-H largely disappeared from the microstructure. The lack of M-S-H, accompanied with the abundant presence of SiO_2 particles, where MS-C sample differed from the corresponding MS-S sample that was cured under ambient conditions, could be an indication of the conversion of Mg-based initial phases to Mg-carbonates under the presence of CO_2 curing.

Figure 6.4 FESEM images of (a) M-S, (b) M-C, (c) MS-S and (d) MS-C samples at 28 days

6.3.4. XRD

The XRD diffractograms of all samples cured for 3 days are shown in Figure 6.5. The brucite peaks were accompanied with unreacted MgO (periclase) peaks in all samples, whose presence was an indication of the limited progress of hydration during the first 3 days of curing. The M samples, whose binder component was composed of MgO only, demonstrated brucite peaks with noticeably higher intensities than those of MS (MgO-SiO₂) samples. This difference in the brucite peaks could be attributed to the higher initial MgO content of the M samples when compared to MS samples (40 vs. 20 wt% of

the total mix composition) and the potentially higher consumption degree of the brucite that may have initially formed within the MS system, via its reaction with the dissolved silica to form M-S-H and carbonation (in the MS-C sample).

Apart from MgO and brucite, the presence of small amounts of silica and magnesite (the latter from the incomplete decomposition of the parent material during the production of MgO) was observed as impurities in all samples. While the XRD patterns of MS-S and MS-C were similar, a small presence of hydromagnesite/dypingite was observed in MS-C samples, which was in line with the microstructural observations reported earlier in Section 6.3.3. These were accompanied with unreacted amorphous silica peaks centered around $21^\circ 2\theta$. The slight formation of amorphous M-S-H was observed at around 35° and $60^\circ 2\theta$ (T. Zhang et al., 2011a; T. Zhang et al., 2014b) in both MS samples, albeit more visibly within the MS-S sample. This difference was associated with the variations in the environments used for the curing of these samples, during which MS-C was subjected to carbonation. The use of carbonation curing limited the formation of M-S-H and resulted in the slight presence of carbonates instead, similar to M-C samples. Although the formation of carbonate phases within M-C and MS-C samples was clearly observed in their microstructures reported in Section 6.3.3, these phases did not reveal high intensities in the XRD patterns obtained at 3 days. This could be due to the relatively lower intensities of these phases in comparison to major phases such as MgO and brucite and the variations in the carbonation degree, which reduced with sample depth. These results can be an indication that although the progress of carbonation was limited in M-C and MS-C samples, it still significantly enhanced the mechanical performance of these samples in comparison to the corresponding uncarbonated samples at as early as 3 days.

Figure 6.6 shows the XRD diffractograms of all samples cured for 28 days. Although the presence of MgO could still be observed in all samples, a

reduction in its intensity was anticipated in comparison to those observed at 3 days to demonstrate the progress of hydration and carbonation between these periods. While the brucite peaks were present in all samples, they were less prominent within samples subjected to carbonation for each composition. The brucite peaks were accompanied with various HMCs such as hydromagnesite, dypingite, artinite and nesquehonite within M-C samples, which corresponded well with microstructural observations. Alternatively, the amorphous bands of M-S-H located at around 25° , 35° and 60° 2θ (Z. Li et al., 2014c) were clearly revealed in the XRD pattern of MS-S samples. In addition to M-S-H, small peaks of MgO and brucite were also present within MS-S, indicating that there was still room for improvement for the complete utilization of MgO. Subjecting the same composition to carbonation led to the disappearance of brucite and the reduction in the amount of residual MgO in MS-C samples. The simultaneous appearance of various HMCs was a clear demonstration of the carbonation reaction within the MgO-SiO₂ system. The lack of M-S-H peaks, accompanied with the presence of unreacted silica at around 21° 2θ within MS-C samples indicated the conversion of Mg-phases into carbonates under carbonation curing, which confirmed the microstructural observations (Section 6.3.3) and strength results (Section 6.3.2) reported earlier.

Figure 6.5 XRD diffractograms of all samples at 3 days

Figure 6.6 XRD diffractograms of all samples at 28 days

6.3.5. TG/DTG

Figure 6.7 shows the TG and DTG plots of all samples cured for 28 days. Since all samples were subjected to vacuum drying before testing, the total mass loss observed during this process mainly corresponded to the decomposition of hydrate and carbonate phases. When the total mass loss values revealed by each sample were compared, it could be seen that MS-S sample revealed lower values than others. This difference could be partially attributed to the higher initial MgO contents of M samples in comparison to MS samples, which could have led to the formation of a larger amount of hydrate and/or carbonate phases. Furthermore, the formation of carbonate phases within sample MS-C led to a higher mass loss than those of MS-S. Regardless of the initial composition, amongst each binder composition (MgO and MgO-SiO₂), those subjected to carbonation led to higher mass losses due to the decomposition of HMCs. In carbonated MgO systems, the dehydration, dehydroxylation and decarbonation of common HMCs (e.g. nesquehonite, artinite, hydromagnesite and dypingite) were reported to take place at < 250, 250-500, and > 350 °C, respectively (Bhattacharjya, Selvamani, & Mukhopadhyay, 2012; Hollingbery & Hull, 2010; Lanas & Alvarez, 2004; Vágvölgyi et al., 2008). In MgO-SiO₂-H₂O systems, the main steps involved during the thermal decomposition of M-S-H and other phases can be summarized as below (Lothenbach et al., 2015; Nied et al., 2016):

1. 30-300 °C: Loss of interlayer water of M-S-H
2. 300-750 °C: Decomposition of uncarbonated brucite and separation of hydroxyl groups in M-S-H
3. 750-900 °C: Dehydroxylation of silanol groups

(a)

(b)

Figure 6.7 Thermogravimetric analysis results of all samples at 28 days, showing the (a) TG and (b) DTG plot

Amongst the samples cured under sealed conditions, the much lower mass loss of MS-S than that of M-S was accompanied with its higher strengths than sample M-S. This difference in the strengths of these two uncarbonated samples could be linked with the variations in the hydrate phases that formed within the MgO (brucite) and MgO-SiO₂ (M-S-H with a minor formation of brucite) formulations. This variation was also demonstrated by the DTG plots in Figure 6.7 (b), where the two peaks at 95 and 405 °C within MS-S sample referred to the loss of interlayer water and separation of hydroxyl groups of M-S-H along with the decomposition of a small amount of brucite, respectively. Alternatively, the thermal decomposition of M-S sample revealed a large endothermic peak at ~425 °C corresponding to the decomposition of brucite, which was in line with the XRD patterns shown in Figure 6.6. When the 28-day strength results of these two samples were compared, the larger contribution of M-S-H to the strength development of MS-S sample than that of brucite, whose extensive formation was clearly observed in M-S sample, could be confirmed.

The introduction of carbonation at a CO₂ concentration of 10% during the curing of M-C and MS-C samples led to the appearance of additional peaks associated with the formation of carbonate phases. The DTG plots of these samples revealed two additional endothermic peaks centered at around 224-263 and 491-507 °C, corresponding to the dehydroxylation and decarbonation of HMCs, respectively. Furthermore, when compared to the DTG plots of uncarbonated M-S and MS-S samples, a slight shift in the main decomposition peak from 405-425 to 434-438 °C was observed in the carbonated samples, which included the decomposition of carbonate phases. These decomposition patterns corresponded well with the temperature ranges stated in the literature (Lanas & Alvarez, 2004; Vágvölgyi et al., 2008). The decomposition temperatures and corresponding mass loss values revealed by the TG/DTG analysis were used to quantify the hydrate and carbonate phases within each sample, whose details are provided in Section 6.3.6.

6.3.6. Phase quantifications

Figure 6.8 (a)-(d) show the deconvoluted DTG curves for all samples cured for 28 days. The original data (represented by the black dots) was included as well as the cumulative fit (represented by the solid line) for each sample, showing that a good fit was obtained in all cases. These two sets were accompanied with the deconvoluted curves, whose combination formed the cumulative fit. For each sample, the number of deconvoluted curves varied, depending on the different types of hydrate and carbonate phases that decomposed during thermal analysis. For instance, for M-S sample, two main curves were used to represent the dehydration of adsorbed water (centered at ~ 128 °C) and dehydroxylation of brucite (centered at ~ 425 °C), along with the loss on ignition associated with impurities (e.g. undecomposed phases within MgO). In addition to these curves, two more curves (centered at ~ 263 and ~ 491 °C) were added to represent the mass loss associated with the decomposition of HMCs within M-C sample. Furthermore, the main curve (centered at ~ 430 °C) was deconvoluted into two curves that corresponded with the decompositions of brucite (centered at ~ 407 °C) and HMCs (centered at ~ 437 °C).

Differing from the M samples, MS samples included the decomposition of M-S-H in addition to other hydrate and carbonate phases. For MS-S sample, the three main phases referred to the dehydration of adsorbed water from M-S-H, dehydroxylation of brucite and dehydroxylation of M-S-H. While each of these 3 events was indicated by separate curves, the dehydration of M-S-H was represented by two individual curves referring to the water adsorbed on M-S-H surface and water confined in M-S-H pores (M Tonelli et al., 2016). For MS-C sample subjected to carbonation, 2 more curves were used to represent the dehydroxylation and decarbonation of HMCs (at ~ 224 and ~ 507 °C), in addition to the 3 decomposition reactions listed earlier for MS-S sample. Similar to M-C sample, the main curve (centered at ~ 434 °C) was divided into two to represent the decompositions of brucite and HMCs, in line with the findings of the previous literature on the thermal decomposition of HMCs (Hollingbery & Hull, 2010; Jauffret, Morrison, & Glasser, 2015). The area under each deconvoluted curve was calculated to find the mass loss corresponding to the

relevant decomposition processes. During these calculations, the mass loss associated with the loss of ignition was also taken into account with respect to the binder component within each sample.

Figure 6.8 Deconvolution of DTG curves of (a) M-S, (b) M-C, (c) MS-S and (d) MS-C samples at 28 days

The mass loss values obtained from the deconvoluted DTG curves of all samples cured for 28 days are listed in Table 6.2. Similar to the phase formations shown by the XRD patterns in Figure 6.6 , M-S sample revealed the formation of brucite as the main hydrate phase, which corresponded to ~20% of the total mass loss. The high

brucite content within this sample was an indication of the lack of carbonation, whose progress was limited under the ambient CO₂ concentration used during the curing of M-S. The introduction of carbonation in M-C sample led to the formation of HMCs (mass loss of ~14%), in addition to brucite (mass loss of ~5%). The smaller brucite content of M-C when compared to M-S revealed the progress of carbonation under the elevated (10%) CO₂ concentration used during the curing of M-C. Differing from sample M-S, a majority of brucite that formed as a result of the hydration reaction reacted with the CO₂ that diffused through the pore system, resulting in a notable formation of HMCs.

Table 6.2 Allocation of mass loss revealed during the thermal decomposition of samples cured for 28 days, based on the deconvoluted DTG curves.

Sample	Mass loss (% of original mass)			
	Adsorbed water (dehydration)	Brucite (dehydroxylation)	M-S-H (dehydroxylation)	HMCs (dehydroxylation/ decarbonation)
M-S	2.2	19.9	-	-
M-C	2.4	5.1	-	14.2
MS-S	7.3	2.8	6.4	-
MS-C	4.2	0.5	2.2	19.0

Similar to M samples, MS samples indicated different mass allocations with respect to their curing environments. MS-S sample indicated a high mass loss associated with the dehydroxylation of M-S-H (~6%), along with smaller amounts due to the dehydroxylation brucite (~3%). Out of all samples, MS-S revealed the highest mass loss due to adsorbed water, which was an indication of M-S-H formation. This was

because dehydration of water absorbed on the surface of M-S-H as well as the water confined in M-S-H pores are known to contribute to the mass loss observed in this temperature range (M Tonelli et al., 2016). The use of carbonation in MS-C sample enabled a reduction of the amount of residual brucite (mass loss of ~0.5%), which almost disappeared at 28 days. This decline in the amount of brucite was related with its consumption in the formation of carbonate phases, along with M-S-H. Accordingly, the main mass loss observed in MS-C was linked with a significant formation of HMCs (mass loss of ~19%), accompanied with some M-S-H (mass loss of ~2%). The smaller amount of M-S-H formation within sample MS-C in comparison to MS-S, which corresponded well with the XRD patterns, could be associated with the utilization of Mg^{2+} in the carbonation reaction rather than its reaction with SiO_2 complexes to form M-S-H.

The reactions involving the formation of various hydrate and carbonate phases are dependent on several factors, one of them being the pH of the system, which can determine the dissolution of MgO and SiO_2 , as well CO_2 into the pore solution. Therefore, the direction of the reactions that determine the M-S-H and HMC contents within carbonated MS systems are controlled by the concentration of the dissolved SiO_2 and CO_2 , during which the dissolved element with the higher concentration preferentially reacts with Mg^{2+} . In this respect, the rate and degree of the reactions depend on the concentration of the dissolved element and the solubility product of M-S-H and HMCs. In this study, the overwhelming formation of HMCs when compared to M-S-H in MS-C samples could be attributed to the higher dissolution of CO_2 gas (i.e. at a concentration of 10%) than that of solid SiO_2 . Furthermore, the lower pH values induced with carbonation could have also enhanced the formation of HMCs (Ballirano, De Vito, Mignardi, & Ferrini, 2013; Vincenzo Ferrini, Caterina De Vito, & Silvano Mignardi, 2009) rather than M-S-H, whose formation was shown to be favored at a higher pH of ≥ 10.5 (Z. Li et al., 2014c; Monica Tonelli et al., 2017).

A comparison of the two carbonated samples, M-C and MS-C, revealed lower mass loss values corresponding to the formation of HMCs within the former (~14% vs. 19%). This difference in the amount of carbonate phases could be related to the variations in the type of carbonates, as well as the higher initial densities of M samples in comparison to MS samples, which could limit the amount of CO₂ diffusing through the sample pore network and thereby the overall amount of carbonates precipitating within the system. However, although M-C samples revealed a lower degree of carbonate formation, their higher densities enabled them to achieve generally higher strengths than MS-C samples during the earlier stages (≤ 28 days) of carbonation. The increased degree of carbonate formation within MS-C samples, coupled with the binding strength provided by M-S-H, led to almost equivalent strengths to those of M-C samples at 56 days (73 vs. 79 MPa). These results indicate that while sample density plays a key role in the reaction mechanisms and final performance, the progress of the carbonation reaction also contributes to strength development via the formation of an extensive carbonate network.

In addition to their physical properties, other factors such as the initial pH (i.e. controlled by the mix design and properties of the binder component), determine the extent of carbonation and hence the final performance of M and MS systems. The presence of SiO₂ has led to a lower initial pH of MS when compared to M samples, which may have provided a more favorable environment for HMC formation under carbonation (Ballirano et al., 2013; Vincenzo Ferrini et al., 2009). Furthermore, in purely MgO-based systems (M-C samples), the hydration and carbonation of MgO grains can lead to the formation of a solid hydrate/carbonate layer around the unreacted particles, thereby limiting further access to the unhydrated MgO particles. However, in MgO-SiO₂ systems (MS-C samples), since the dissolution of SiO₂ is lower than that of CO₂ under the given conditions, the presence of SiO₂ particles can provide nucleation seeding. This can enable the increased precipitation of Mg(OH)₂ available for carbonation, thereby facilitating further carbonation and the associated formation of HMCs when compared to M samples.

6.4. Conclusions

This study investigated the strength and microstructural development of MgO and MgO-SiO₂ binder systems under different curing conditions. Concrete samples, whose binder component consisted of only MgO or MgO-SiO₂ were subjected to ambient and carbonation curing conditions for 56 days. The compressive strength results were supported with microstructural analysis performed via XRD, TG/DTG and FESEM. While the formation of brucite within MgO samples led to limited strength under ambient conditions, MgO-SiO₂ samples demonstrated a steady strength development due to the formation of M-S-H. Incorporation of carbonation curing enhanced the mechanical performance of both systems, enabling rapid strength development that reached up to 77 MPa at 7 days. This increase in strength was associated with the densification of microstructure via the formation of Mg-carbonates, which were assessed via thermal analysis.

The strength development of MgO samples was faster in comparison to MgO-SiO₂ samples. The ultimate strength was determined within 7 days for MgO samples, whereas for MgO-SiO₂ samples strength development still continued after 56 days. This difference in strength development between MgO and MgO-SiO₂ samples was due to different strength gaining mechanisms for each sample. MgO samples rely on carbonation to gain high strengths while MgO-SiO₂ samples strength gaining mechanism is based on hydration. The rapid strength development for MgO samples makes them ideal choices for applications that require fast manufacturing and installation. On the other hand, the major disadvantage of MgO samples in comparison to MgO-SiO₂ samples is the required carbonation curing; whereas MgO-SiO₂ samples do not necessarily need carbonation curing. The obligation of carbonation curing makes MgO samples not suitable for on-site casting but rather more suitable for prefabrication while MgO-SiO₂ samples can be cast and cured on-site as well. Nevertheless, for both MgO and MgO-SiO₂ samples a good level of workability and satisfactory mechanical performances were able to be achieved under appropriate conditions.

Chapter 7: DURABILITY AND ASSOCIATED PERFORMANCE OF MgO-SiO₂ BASED CONCRETE UNDER VARIOUS ENVIRONMENTS

7.1. Introduction

Although the reaction mechanisms, properties and mechanical performance of MgO-SiO₂ systems have been previously investigated, the durability aspects of this binder system under severe environments remain to be reported. In line with this gap in the literature, this chapter aims to investigate the performance of MgO-SiO₂ based binders under different environments, whose influence on strength development was evaluated via a comparison of MgO-SiO₂ and PC-based concrete samples subjected to the same environments. The prepared samples were subjected to sealed, under water, carbonation, sodium chloride (NaCl), magnesium chloride (MgCl₂) and magnesium sulfate (MgSO₄) environments for up to 180 days. This was followed by an assessment of their mechanical performance via compressive strength testing at different durations and pH measurements. The strength results of MgO-SiO₂ samples were supported with a detailed microstructural analysis at different stages of exposure. The formation of phases was investigated via X-ray diffraction (XRD) and thermogravimetric/derivative thermogravimetric analysis (TG/DTG), while the microstructural observations were performed via field emission scanning electron microscopy (FESEM).

7.2. Mix details and curing conditions

Table 7.1 presents the mix compositions of the 50 mm cubic samples prepared in this study. M samples were composed of MgO and MS at a ratio of 1.5:1. P samples were composed of PC as their main binder component. The M and P samples were composed of 40% binder and 60% coarse aggregates by mass. Fine aggregates were not included in this mix design to avoid any quartz contamination during microstructural analysis. Both M and P systems were prepared with a constant water/binder (w/b) ratio of 0.4. M samples included 2% (i.e. of the total binder

content) of SHMP to improve their fluidity, in line with the findings of previous studies (Tran & Scott, 2017; J. Wei, Chen, & Li, 2006).

Table 7.1 Mix compositions used in this study

Sample	Dry mix (wt.%)				SHMP
	MgO	PC	MS	Coarse	
M	24	-	16	60	2%
P	-	40	-	60	-

After 28 days of curing under sealed conditions, the prepared samples were subjected to five different durability environments in addition to a control (sealed) environment. The details of the durability environments are as follows: (i) sealed/control (C) under 95% relative humidity (RH) and ambient CO₂ concentration; (ii) carbonated (CA) under 95% RH and 10% CO₂ concentration; (iii) under water (W); (iv) under sodium chloride (SC) solution at 10mg/L concentration; (v) under magnesium chloride (MC) solution at 10mg/L concentration; (vi) under magnesium sulfate (MSu) solution at 10mg/L concentration. All conditions were maintained under an ambient temperature of 28 ± 2 °C. The solutions were renewed every 3 weeks to avoid the solution concentrations to drop due reactions with the samples.

7.3. Results and Discussion

7.3.1. Compressive strength

The compressive strengths of M and P samples exposed to different durability conditions for extended periods up to 180 days are shown in Figure 7.1 and Figure 7.2, respectively. Before being subjected to different durability conditions, the 28-day compressive strengths of M and P samples were recorded as 65 and 55 MPa,

respectively. This higher initial 28-day strength achieved by M samples in comparison to P samples was associated with the water content used in both mixes. Although the w/b ratio was kept constant at 0.4 for consistency within both M and P systems, this water content led to slightly wet mixes for P samples, as the amount of water required by PC to achieve a standard consistency is lower than MgO (i.e. 0.28 vs. 0.64) (Jin & Al-Tabbaa, 2014b; Lemonis et al., 2015). While the formation of M-S-H was the main source of strength within M samples, the strength development of P samples was attributed to the formation of calcium-silicate-hydrate (C-S-H) and calcium hydroxide (CH).

Figure 7.1 Compressive strength of M samples under different conditions

Figure 7.2 Compressive strength of P samples under different conditions

When subjected to curing under a sealed environment for up to 180 days, the control (C) samples within both M and P systems exhibited a continuous strength gain, which was an indication of the continuation of the hydration reaction after 28 days of initial curing. M samples demonstrated an increase in strength up to 90 days by reaching 84 MPa, which remained relatively stable up until 180 days. Alternatively, P samples showed a continuous increase in strength up until 180 days and reached 74 MPa. Under the sealed environment used in the curing of the control samples, M samples achieved higher strengths than P samples at all durations. This increased performance of M samples was associated with the continuous formation of M-S-H under sealed conditions, which were more favorable for M samples. These strength

values obtained under the control environment were used as a benchmark value to compare the performance of each system under various durability environments.

The use of carbonation (CA) was favorable in terms of the compressive strength development of both M and P samples. Amongst all the durability conditions they were subjected to, M samples achieved the highest strengths (80 MPa from 56 days onwards) under carbonation throughout the 180 days of curing. The strength gain exhibited by these samples was associated with the formation of Mg-based carbonate phases that are known to be the main source of strength within carbonated MgO systems (Dung & Unluer, 2017b; Martin Liska & Abir Al-Tabbaa, 2009; M. Liska et al., 2008). Alternatively, P samples exhibited a continuous strength gain under carbonation and reached over 90 MPa at 180 days. Similar to M samples, this increase in strength was attributed to the formation of calcite under these accelerated carbonation conditions (i.e. 10% CO₂ concentration) and the associated reduction in sample porosity via the expansive formation of carbonate phases.

M samples subjected to under water (W) curing revealed the lowest strengths amongst all the durability conditions. The strengths of these samples remained at around 65 MPa, which was similar to the strength observed after the 28 days of initial curing, during the entire testing period of 180 days. The lack of further strength development after 28 days of initial curing could be due to the leaching of ions in water, which was previously reported for M-S-H samples cured under water (Jin & Al-Tabbaa, 2014b). The adverse effect of water curing for M samples could be an indication of dimensional stability issues within M-S-H samples (Jia et al., 2016). On the contrary, P samples cured under water demonstrated a steady strength development and outperformed the control sample by reaching 80 MPa at 180 days. For P samples, the increase in compressive strength was due to the continuation of the hydration reaction in the presence of water, as expected.

When subjected to sodium chloride (SC) solution, M samples revealed the second lowest strength values after the W environment throughout the entire duration. Although there was not a reduction in strength when compared to the initial 28-day

strength, M samples exhibited a very limited strength development up to 90 days and reached ~72 MPa, which remained stable until 180 days. These values were lower than those of the control sample, which achieved ~16% higher strengths than those subjected to SC at 180 days. The lower strength development under SC environment could be attributed to the limited formation of M-S-H and the development of a new phase (e.g. magnesium chloride, MgCl_2) from the Mg^{2+} ions released from the sample and Cl^- from the testing solution. Similar to M samples, SC environment inhibited strength gain in P samples, which could only achieve ~8 MPa of strength increase after the initial 28 days. P samples kept under SC environment for 180 days revealed a strength value of 63 MPa, which was notably lower than that of the samples under C, CA and W environments. These lower strengths of P samples under SC could be due to the dissolution of C-S-H and CH and formation of calcium chloride (CaCl_2) (Sutter et al., 2006).

Under magnesium chloride (MC) environment, M samples exhibited a gradual increase in strength up to 90 days and reached a compressive strength value of ~77 MPa, after which a slight reduction in strength to ~74 MPa was observed at 180 days. M samples subjected to MC environment revealed intermediate strengths that were generally higher than those of W and SC environments. Compared to the control sample at 180 days, a 11.5% reduction in strength was observed in MC environment. These lower strengths could be attributed to volume stability issues caused due to curing in solution. Alternatively, P samples exhibited a significant decrease in strength under MC environment, which was immediately obvious from the first few days of testing. The compressive strength of P samples reduced by ~16% on average when compared the initial 28-day strength and remained at ~46 MPa for the entire testing period. The detrimental effect of MC solution on P samples could be attributed to the depletion of CH and decalcification of C-S-H (Gégout, Revertégat, & Moine, 1992). Additionally, calcium oxychloride ($3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}$), which generates hydraulic pressure on cement matrix, could have formed in the presence of Cl^- ions (Monosi & Collepardi, 1990). When the two systems were compared, the higher durability of M samples when compared to P samples under MC environmental could be easily observed. This difference in performance could be

associated with the lower solubility of the hydrate phases in MgO-SiO₂ systems (i.e. brucite and M-S-H), when compared to those in PC systems (i.e. CH and C-S-H). Solubility of brucite is 0.009 g/L at 18 °C, while this value is 1.23 g/L for CH (P Kumar Mehta & Monteiro, 2006; Shand, 2006).

Under magnesium sulfate (MSu) environment, M samples achieved a considerable increase in compressive strength, reaching ~77 MPa at 180 days, which was 7% lower than the control sample. However, when compared to W, SC and MC environments, samples subjected to MSu environment revealed higher strengths at all times, which could be due to the increased amount of Mg²⁺ ions in solution that could have contributed to the formation of M-S-H (David Bonen & Menashi D. Cohen, 1992). The compressive strength values of P samples under MSu environment was affected in a similar manner to those subjected to MC, albeit not at the same scale. P samples kept under MSu environment indicated an average of ~2% reduction in the strength values when compared to the initial 28-day curing strength, which was better than those observed in MC environment. This low reduction in strength could be attributed to the formation of gypsum and ettringite, and the decline in the amount of CH formed (Maes & De Belie, 2014). Similar to MC environment, the higher durability of M samples under MSu environment led to strength gain, whereas a deterioration was revealed in P samples due to the differences in the reaction mechanisms and phase formations observed within each system.

Collectively, the changes in the strength development of each system demonstrated the durability of M and P samples individually under different conditions. While both sets of samples contained to gain strength under sealed (C) and carbonation (CA) environments due to the densification of the sample structure via the continuation of hydration and carbonation reactions, the use of under water (W) curing as well as SC, MC and MSu solutions led to variations in sample performance. Both systems indicated a slight increase in strength in SC solution. Under water curing was beneficial for the strength development of P samples, which benefitted from the

continuation of hydration; whereas M samples demonstrated a lack of strength gain that could be associated with dimensional stability issues. When compared to P samples, M samples revealed higher resistance under MC and MSu solutions, which was attributed to the formation of M-S-H and brucite under the increased concentration of Mg^{2+} and their lower solubility values in comparison to Ca-based hydrate phases.

7.3.2. pH

The pH values of M and P samples exposed to different durability conditions for 90 days are shown in Figure 7.3. The initial 28-day values (I-28) of M and P samples before the start of durability testing were recorded as 10.6 and 12.7, respectively. Previous studies (Z. Li et al., 2014a; T. Zhang et al., 2011a) showed that a pH value of around 10 was observed in MgO-SiO_2 samples after 28 days of hydration. The slightly higher pH values observed for M samples in this study could be attributed to the presence of impurities in MgO and formation of brucite, which has a pH value of ~ 10.5 . For PC systems, hydration results in a pH value between 12 and 13 (P Kumar Mehta & Monteiro, 2006), which was in line with the initial measurement. When the pH values of M and P samples were compared over the 90 days of exposure, M samples had significantly lower pH values than P samples under all durability conditions due to the different binders used in each system.

When compared to the control sample at 90 days, M samples revealed very similar pH values under most of the durability conditions such as CA, MC and MSu, which could be an indication of the stability of formed phases under each of these conditions. The only two conditions that indicated the largest deviation was the SC solution and under water curing. When subjected to SC, an increase in pH was observed; whereas those cured under water led to slightly lower pH values than the control. This reduction in pH could be attributed to the leaching of ions under water. The higher pH value of M samples under SC environment, which was also observed in MC solution to a smaller extent, could indicate the formation of a new phase,

which could explain the reduction in strength compared to the control sample.

Alternatively, a significant reduction in the pH values of P samples subjected to MC environment was observed, which was in line with the lowest strength results of these samples. This reduction was associated with the consumption of CH and decalcification of C-S-H. Other than the MC environment, most other environments revealed relatively similar pH values to the control. The slight reduction observed under CA was in line with the progress of the carbonation reaction. Although not at the same scale as the MC solution, subjecting P samples to SC and MSu solutions also led to lower pH values than the control, which explained the lower strengths of P samples under these solutions in comparison to the control sample at 90 days. When compared to M samples, P samples generally indicated a larger deviation from the pH of the control sample, which could be an indication of the higher stability of M samples to various conditions.

Figure 7.3 pH values of M and P samples under different conditions

7.3.3. Microstructure

Figures 7.4 and 7.5 show the FESEM images of M samples after being subjected to different durability conditions for 28 and 90 days, respectively. Both figures also include the FESEM image of the initial sample at 28-days (I-28) to illustrate the morphology of M samples before they were subjected to any environment. The formation of M-S-H gel that formed a continuous network, along with spherical silica pores, could be observed in the I-28 sample. A similar microstructure was revealed by the control sample (C) at 28 and 90 days, during which the presence of M-S-H layer dominated the microstructure. This was an indication of the continuation of the hydration reaction, thereby explaining the gradual increase in the compressive strength of the control sample over time.

M samples subjected to carbonation (CA), shown in Figures 7.4 (c) and 7.5 (c), possessed a similar microstructure to the control sample, with some arguable densification as less silica pores were observed. Formation of any carbonate phases such as hydrated magnesium carbonates (HMC) were not observed by FESEM, which suggests that the conversion of Mg-phases such as M-S-H to carbonates was limited even after 90 days of carbonation. These findings differed from those reported in a previous study (C. Sonat & C. Unluer, 2017), where the formation of HMCs was widely observed and associated with strength gain in MgO-SiO₂ samples subjected to carbonation immediately after casting. The lack of HMC formation in this study was associated with the introduction of carbonation after 28 days of curing in a sealed environment, after which the diffusion of CO₂ through the dense hydrate network and its reaction with hydrate phases was limited.

When M samples were subjected to under water (W) curing, a reduction in the continuity of M-S-H layer was observed in Figures 7.4 (d) and 7.5 (d). This reduction in M-S-H was accompanied with an increase in the amount of individual particles, which could be identified as brucite and MgO. Delayed formation of brucite may have led to dimensional stability problems, thereby resulting in the formation of cracks, as can be seen in Figure 7.6 (b). These changes in the microstructure could explain the

hindered strength development of these samples. Similar to under water curing, M samples subjected to SC environment led to a disintegrated microstructure at 28 days (Figure 7.4 (e)), resulting in the disturbance of the continuous M-S-H previously observed at 28 days, before the start of the durability test. However, a different scenario was revealed at 90 days (Figure 7.5 (e)), during which the formation of a new phase with a distinct morphology, involving particles with larger sizes and rough surfaces, was observed.

As seen in in Figures 7.4 (f) and 7.5 (f), M samples subjected to MC environment led to similar microstructures as the control samples at both curing durations, where a continuous and dense layer of M-S-H was generally observed. Under MSu environment (Figures 7.4 (g) and 7.5 (g)), the formation of a new phase, identified by round dark spherical bulky particles, was seen around the sample microstructure. The presence of these particles was more pronounced at 90 days, showing that their formation continued under the longer exposure to MSu environment. The dispersed formation of these distinct phases around the continuous layer formed by M-S-H gel could explain the lower strength results of these samples when compared to the control sample at 90 days.

Figure 7.4 FESEM images of M samples under various conditions: (a) I-28, (b) C, (c) CA, (d) W, (e) SC, (f) MC and (g) MSu at 28 days

Figure 7.5 FESEM images of M samples under various conditions: (a) I-28, (b) C, (c) CA, (d) W, (e) SC, (f) MC and (g) MSu at 90 days

Figure 7.6 Images showing samples under (a) control and (b) under water environments at 90 days

7.3.4. XRD

The XRD diffractograms of M samples exposed to different durability conditions for 28 and 90 days are shown in Figures 7.7 and 7.8, respectively. There were notable similarities in the XRD patterns of most samples at 28 and 90 days. The presence of unhydrated MgO (i.e. periclase) and brucite was observed in all samples, along with the presence of amorphous M-S-H at $\sim 20\text{-}30^\circ$, $\sim 35^\circ$, and 60° 2 Theta. Additionally, quartz was observed in most samples due to the contamination from coarse aggregates in the preparation of powder samples for XRD analysis. The main unreacted periclase peaks, located at 43° and 63° 2 Theta, indicated that the hydration of MgO was not complete at both durations, which was in line with the findings of earlier studies (C Sonat & C Unluer, 2017; Jacek Szczerba et al., 2013).

When compared to the periclase peak within the I-28 sample, the intensity of this peak reduced in all samples subjected to different conditions. This reduction was more pronounced at 90 days, indicating the continuation of the hydration reaction after the initial 28 days of curing. Alternatively, no obvious change in the presence of

brucite peaks was observed in most samples, except for a slight increase revealed by M samples subjected to under water curing. This increase could be an indication of the higher degree of brucite formation within these samples, which could explain the formation of cracks and lower strength results of these samples than others at later ages. Differing from brucite, the presence of the main hydrate phase of MgO-SiO₂ systems, M-S-H, could explain the strength development of M samples over time. The lack of any notable change in the characteristic peaks of M-S-H, even after 90 days of exposure, was an indication of its stability under various conditions including carbonation, sulphate and chloride attack.

Figure 7.7 XRD diffractograms of M samples at 28 days

Figure 7.8 XRD diffractograms of M samples at 90 days

7.3.5. TG/DTG

TG plots of M samples exposed to different durability conditions for 28 and 90 days are presented in Figures 7.9 (a) and (b), respectively. DTG plots of the same samples are also shown in Figures 7.10 (a) and (b). The total mass loss obtained in all samples was mainly due to the decomposition of brucite and M-S-H, which were the two main hydration products observed within the $\text{MgO-SiO}_2\text{-H}_2\text{O}$ system. In line with the findings of previous studies (C Sonat & C Unluer, 2017; Jacek Szczerba et

al., 2013; T. Zhang et al., 2014b), all samples followed a systematic mass loss throughout the temperature range they were exposed to, during which a steep decrease around ~ 400 °C was revealed, which referred to brucite dehydroxylation. Other than brucite, the following decomposition reactions are observed in the thermal decomposition of MgO-SiO₂-H₂O systems (Lothenbach et al., 2015; T. Zhang et al., 2014b):

1. 30-300 °C: Loss of interlayer water of M-S-H
2. 300-750 °C: Decomposition of brucite and separation of hydroxyl groups in M-S-H
3. 750-900 °C: Dehydroxylation of silanol groups

Most samples, except for those subjected to under water (W) curing, revealed similar mass loss values at 28 days (Figure 7.9 (a)). The notably lower total mass loss of W sample at 28 day was reflected in its lower compressive strengths. Differing from the trend observed in 28 days, all samples revealed similar mass losses at 90 days (Figure 7.9 (b)), which suggested that M samples were not significantly affected by various durability environments they were subjected to even after 90 days. The increase in the mass loss of samples cured under water at 90 days could be associated with the increased formation of brucite at later ages, which was also observed earlier in the XRD patterns.

For a detailed investigation of the decomposition of the different phases, the deconvoluted first derivatives of the TG curves (DTG) were generated. The DTG plots shown in Figure 7.10 generally represented similar patterns in all samples subjected to different durability conditions. All samples exhibited three main bands of decomposition reactions, which partially overlapped. The decomposition during 30-300 °C was associated with the loss of interlayer water of M-S-H and the dehydration of the physically bound water, while the decomposition peak centered around 400 °C was characteristic of brucite dehydroxylation. Lastly, the broad hump occurring just after the brucite decomposition (~ 550 °C) was indication of M-S-H dehydroxylation. When compared to the control sample, the similar DTG curves of all samples under

different durability environments even after 90 days (Figure 7.10 (b)) could be an indication of the stability of the hydration products (e.g. M-S-H and brucite) under different conditions.

(a)

(b)

Figure 7.9 TGA curves of M samples at (a) 28 days and (b) 90 days

(a)

(b)

Figure 7.10 DTG curves of M samples at (a) 28 days and (b) 90 days

Figures 7.11 and 7.12 show the deconvoluted DTG curves of M samples under different durability conditions for 28 and 90 days, in addition to those of the I-28

sample. The original data (represented by the black dots) was included as well as the cumulative fit (represented by the thick solid line) for each sample, showing that a good fit was obtained in all cases. These two sets were accompanied with the deconvoluted curves, whose combination formed the cumulative fit. Each deconvoluted curve, represented different decomposition reactions observed during thermal analysis. The two curves at up to 300 °C represented the dehydration of interlayer water of M-S-H and dehydration of physically bound water within all samples. It is known that M-S-H loses physically bound water in this temperature range, therefore this range can be attributed to the adsorbed water in the sample as well as the loss of interlayer water in M-S-H. The relatively tall curve around 400 °C indicated the dehydroxylation of brucite in all samples. The remaining curves were used to describe the dehydroxylation of M-S-H over the whole temperature range. This range also included the mass loss associated with the loss on ignition of the raw materials, which could have led to the overestimation of the mass loss due to M-S-H dehydroxylation. However, as all samples followed the exact same binder and initial mix composition, the effect of loss on ignition on mass loss should be relatively constant within all samples.

The mass loss values revealed from the deconvolution curves of M samples under different durability conditions at 28 and 90 days are listed in Table 7.2. All the samples exhibited a total mass loss in the narrow range of 19.5-22.2% at both curing durations, except for the W sample at 28 days, whose mass loss remained at 13.9%. When compared to other samples, this limited mass loss was associated with the lower formation of brucite and M-S-H within this sample at 28 days. However, an increase in the mass loss of this sample to 21.1% was observed at 90 days, which could be an indication of increased brucite and M-S-H formation. The delayed formation of these hydrate phases within this sample could have resulted in dimensional stability problems, which was also reflected in its low compressive strength results.

Figure 7.11 Deconvolution of DTG curves of M samples under various conditions: (a) I-28, (b) C, (c) CA, (d) W, (e) SC, (f) MC and (g) MSu at 28 days

Figure 7.12 Deconvolution of DTG curves of M samples under various conditions: (a) I-28, (b) C, (c) CA, (d) W, (e) SC, (f) MC and (g) MSu at 90 days

Table 7.2 Allocation of mass loss obtained from the thermal decomposition of M samples under different durability conditions, based on the deconvoluted DTG curves at 28 and 90 days

Sample	Curing duration (days)	Mass loss (% of original mass)			Total
		Adsorbed water (dehydration)	Brucite (dehydroxylation)	M-S-H (dehydroxylation)	
I-28	28	4.8	2.8	11.9	19.5
C	28+28	6.1	2.7	12.0	20.8
CA		6.5	2.7	12.7	21.9
W		4.0	2.0	7.9	13.9
SC		5.0	2.8	11.8	19.6
MC		6.5	2.5	13.2	22.2
MSu		5.8	2.2	12.3	20.3
C	28+90	6.5	2.3	11.5	20.3
CA		6.8	3.5	11.6	21.9
W		6.5	2.7	11.9	21.1
SC		5.4	2.5	11.6	19.5
MC		6.4	2.7	11.2	20.3
MSu		7.4	2.2	11.1	20.7

All other samples achieved higher mass loss values than the I-28 sample at 28 days, indicating the continuation of hydration after the 28 days of initial curing. Amongst these, those subjected to carbonation (CA) revealed the highest mass loss (21.9%) at 90 days, which could be attributed to the slight formation of carbonate phases under the presence of diffused CO_2 . However, the presence of any carbonate phases did not appear in the form of a significant separate peak in DTG curves, which could be due to the overlap with other phases and the relatively small content of these carbonates, whose presence could also not be detected earlier in XRD and FESEM analyses. Alternatively, samples subjected to SC environment revealed the lowest mass loss at both durations, which could explain their lower strengths results. This outcome could be attributed to the adverse effect of sodium chloride in the hydration of MgO-SiO_2 samples. The appearance of an additional small peak at $\sim 500^\circ\text{C}$ in the DTG plot of SC sample at 90 days (Figure 7.12 (e)) suggested the formation of a new phase, which was in agreement with earlier observations.

Similar to the trend observed in the total mass loss values, mass loss due to the dehydroxylation of brucite and M-S-H was within a narrow range in most samples at both curing durations. While the mass loss due to the decomposition of brucite remained relatively stable over time, a slight reduction in the mass loss due to the dehydroxylation of M-S-H was observed from 28 to 90 days of exposure in most samples. This reduction, albeit small, could be an indication of the changes in the amount of M-S-H at longer exposure durations. However, the lack of any significant change in the mass loss values over time could suggest that the hydration products did not undergo a notable change under the various durability environments used in this study

7.4. Conclusions

MgO-SiO_2 formulations have recently gained significant attention due to the compressive strength levels they achieved and their potential to be utilized in structural/non-structural applications. In addition to strength, the long-term durability

of the MgO-SiO₂ formulations needs to be assured before they can be used in structural applications. This study investigated the durability performance of MgO-SiO₂ based concrete samples under several durability environments including carbonation, NaCl, MgCl₂ and MgSO₄ solutions. Compressive strength of MgO-SiO₂ samples were tested up to 180 days of being subjected to the durability environments after the 28 days of initial curing. For comparison, compressive strength of Portland Cement (PC) based concrete under the same durability environments were tested. Microstructural analysis was performed on MgO-SiO₂ based samples via FESEM, XRD and TG/DTG. Deterioration or depletion of hydration products was not observed for MgO-SiO₂ based samples under any of the environments, whereas PC samples had a reduction in their initial strength under MgCl₂ and MgSO₄ environments. MgO-SiO₂ based concrete was found to have enduring strengths and the potential to be used in structural applications, as long as their dimensional stability concerns are addressed.

Chapter 8: CONCLUSIONS AND FUTURE WORK

8.1. Conclusions

The overall aim of this research was to comprehend the performance of MgO-SiO₂ based formulations through a detailed investigation of key parameters such as mix design, curing conditions, use of alternative materials and durability. This was performed via a combination of various measurement techniques involving mechanical testing and microstructural analysis. The hydration process was analysed via the use of isothermal calorimetry and pH measurements. Compressive strength measurements were executed to assess the mechanical performance of samples at different durations. Microstructural analysis was performed via XRD, TG/DTG, FTIR and FESEM to study the changes in sample structure and composition under different conditions. Several conclusions were drawn regarding the (i) influence of mix design and curing conditions on sample performance and microstructure, (ii) development of M-S-H cements with rice husk ash, (iii) influence of carbonation curing on MgO and MgO-SiO₂ based samples, and (iv) durability and associated performance of MgO-SiO₂ based concrete under various conditions. Main findings from each chapter are summarized in the following section.

8.1.1. Mix composition and curing conditions

The first part of this chapter investigated the influence of mix composition (i.e. MgO/SiO₂ and w/b ratios, and SHMP content) on the workability and mechanical performance of MgO-SiO₂ samples. Paste samples with MgO and SiO₂ contents varying between 30% and 70% were prepared at two different w/b ratios (0.4 and 0.5). M60 sample (60% MgO – 40% SiO₂) at a w/b ratio of 0.4 and M50 sample (50% MgO – 50% SiO₂) at a w/b ratio of 0.5 revealed the highest 28-day strengths. The workability of the MgO-SiO₂ pastes increased with increasing SHMP content at up to 2% (i.e. of total binder by mass), beyond which the workability of pastes was reduced due formation of a bulky structure. The parameters leading to the ideal

design of MgO-SiO₂ formulations were concluded as 50-60% MgO combined with 40-50% SiO₂ and a SHMP content of up to 2%, whereas the w/b ratio was adjusted according to the MgO/SiO₂ ratio. The parameters obtained from this study were utilized in the subsequent studies presented in this thesis.

The second part of this chapter investigated the influence of different curing conditions (i.e. temperature, relative humidity, presence of water and duration) on the hydration and mechanical performance of MgO-SiO₂ binder systems. Performance was evaluated through the hydration mechanism and strength development of the prepared samples. The progress of hydration was assessed by isothermal calorimetry and pH measurements. The amount and structure of the hydrate phases, as well as the microstructure of the prepared samples were analysed via XRD-RIR, TG/DTA, FTIR and FESEM analyses.

The temperature used during the curing process had a direct influence on the hydration mechanisms of MgO-SiO₂ systems. The increase in the initial hydration rate at 60 °C was not sustained over longer durations (> 8 hours), whereas hydration continued for longer durations under 30 °C. Although samples cured under ambient temperatures (30 °C) demonstrated a slow rate of M-S-H formation at early ages, their hydration steadily proceeded over time and resulted in higher M-S-H contents, higher polymerization and denser microstructures at 28 days than those cured under elevated temperatures (60 °C). Samples cured under sealed conditions at ambient temperatures led to the highest 28-day strength results (50 MPa) amongst all samples due to the provision of the required curing conditions for the continuation of the hydration reaction over time. Use of elevated temperatures (60 °C) led to a rapid strength development (34 MPa) at early ages ($\leq$ 3 days), after which a reduction in the strength was observed in the longer durations. The initially high strengths were associated with the accelerated dissolution of MgO and MS and increase in the rate of hydration induced by higher temperatures. This increase in the dissolution of MgO and MS and the rate of the hydration reaction was reflected as a higher degree of M-S-H formation at early ages under 60 °C. This was also observed in the change of

the silicate structure from Q^2 to Q^3 , which was associated with strength development. The rapid early strength gain trend under 60 °C did not continue at longer durations as hydration slowed down and eventually ceased in the absence of the necessary humidity. The reduction in strength in the longer durations under 60 °C was accompanied with lower M-S-H contents and change in M-S-H structure due to the loss of its interlayer water. The Q^3 Si-O structure that initially formed under 60 °C partially transformed to lower polymerization with the reformation of Q^2 Si-O structure in the longer durations, explaining the corresponding strength loss over time. This could be an indication of the dissolution of M-S-H after losing its interlayer water, thereby suggesting the instability and potential disintegration of M-S-H at slightly elevated temperatures.

The outcomes of the different analyses used in this study highlighted the significance of the degree and interconnected structure of the final phase formations on the mechanical performance of the developed formulations. The content of M-S-H as well as its stability under different conditions determined the overall strength development of MgO-SiO₂ binder systems.

8.1.2. Development of M-S-H cements with rice husk ash

This study investigated the performance and microstructural development of MgO-SiO₂ based samples over a 56-day period. Each sample included MgO and a different source of SiO₂, namely microsilica, amorphous RHA and crystalline RHA. The isothermal calorimetry, pH and strength results were supported with microstructural analyses involving XRD, TG/DTG, FTIR and FESEM. In addition to the evolution of sample microstructure, the data corresponding to the quantification of hydrate phases within each formulation, obtained via thermal analysis and XRD-RIR, was used to explain the variations in sample performance.

Samples with crystalline RHA revealed the lowest strengths amongst all samples due to the lack of any reaction between crystalline silica and Mg-phases. Within

these samples, the only hydrate phase that formed was brucite, which did not provide any major binding strength. A different scenario was observed in samples with amorphous silica sources, which achieved higher strengths due to the formation of M-S-H. Samples incorporating amorphous RHA as their silica source exhibited a rapid early compressive strength development reaching 22 and 34 MPa at 3 and 7 days, respectively. Although the formation of M-S-H initially took place at a slower rate when microsilica was used as the silica source, these samples achieved the highest strength, 47 MPa, amongst all samples at 56 days due to the continuous formation of M-S-H. This difference between the formation rate of M-S-H within different samples could be attributed to the variations in the properties and the dissolution rates of various silica sources.

The results of this study clearly demonstrated the potential of amorphous RHA to be utilized as a silica source in MgO-SiO₂ formulations. Samples containing amorphous silica sources reached promising strengths, which were attributed to the development of a dense microstructure enabled by the formation of M-S-H. Amorphous RHA, which is considered as a waste material, can effectively replace microsilica in MgO-SiO₂ formulations, bringing environmental and economic benefits to the production of MgO-based samples.

8.1.3. Influence of carbonation curing on MgO and MgO-SiO₂ based samples

This study investigated the performance and microstructural development of MgO and MgO-SiO₂ based concrete samples subjected to ambient and carbonation curing over a 56-day period. The density and strength results of the prepared samples were supported with a detailed microstructural study involving the use of XRD, TG/DTG and FESEM analyses. In addition to the evolution of sample microstructure, the data corresponding to the quantification of hydrate and carbonate phases within each formulation, obtained via thermal analysis, was used to explain the variations in sample performance.

MgO samples subjected to ambient curing revealed minimal strengths due to the inability of brucite to provide any binding strength between the cement paste and aggregates. A different scenario was observed in MgO-SiO₂ samples, which demonstrated a steady strength development due to the formation of M-S-H over the 56 days of curing. When compared to those cured under ambient conditions, the incorporation of carbonation curing led to an up to 412% and 57% increase in the strength of MgO and MgO-SiO₂ samples, respectively. Unlike the outcome of ambient curing, MgO samples subjected to CO₂ curing exhibited a rapid early strength development revealing strengths as high as 77 MPa at 7 days. This enhancement of performance was associated with the formation of carbonate phases in both MgO and MgO-SiO₂ samples, which led to the densification of sample microstructures. The formation of carbonates was accompanied with a reduction in the amount of hydrate phases in both formulations. The simultaneous formation of different carbonate phases such as nesquehonite, artinite, dypingite and hydromagnesite enabled the development of a dense and interconnected carbonate network within the carbonated samples.

The results of this study clearly demonstrated the critical role carbonation curing plays in the strength and microstructural development of MgO and MgO-SiO₂ formulations. A complete utilization of brucite, the intermediate hydrate phase, was observed in MgO-SiO₂ samples subjected to carbonation, which revealed an extensive formation of Mg-carbonates as well as M-S-H.

8.1.4. Durability and associated performance of MgO-SiO₂ based concrete under various conditions

This study investigated the mechanical performance and microstructural development of MgO-SiO₂ (M) concrete samples subjected to different durability environments over a 180-day period, following 28 days of initial curing. Samples exposed to carbonation, under water curing, and NaCl (SC), MgCl₂ (MC) and MgSO₄

(MSu) solutions were compared with the control sample kept under sealed conditions for the same duration. The changes in the mechanical performance of M samples were also compared to corresponding samples involving the use of PC (P), which were subjected to the same durability environments. The pH and strength results were supported with microstructural analyses involving XRD, TG/DTG and FESEM. In addition to the evolution of sample microstructure, the quantification of hydrate phases within each formulation, obtained via thermal analysis, was used to explain the variations in sample performance under different conditions.

Control samples kept under sealed conditions led to 180-day strengths of 84 and 74 MPa for M and P samples, respectively. Subjecting the samples to carbonation was beneficial for both M and P samples, resulting in high compressive strengths, which were attributed to the densification of microstructure due to the formation of carbonate phases. M samples experienced hindered strength development under water curing potentially due to volume stability issues, while P samples exhibited a notable strength development as water curing enhanced the hydration of PC. Under SC environment the strength development of both M and P samples were lower than those of corresponding control samples. Under MC and MSu environments, M samples revealed continuous strength development over time, albeit lower than the control sample. However, P samples subjected to these two conditions experienced a reduction in their strength, which became more obvious at longer exposure durations.

The results of this study showed that MgO-SiO₂ based concrete samples were overall durable under several aggressive environments, some of which were detrimental for PC samples. Under none of the durability environments used in this study, the strengths of M samples were lowered below the initial 28-day value. The relatively higher strengths obtained by M samples in most conditions were associated with the stability of their hydrate phases, namely brucite and M-S-H. This was confirmed by microstructural analysis, which indicated a lack of any significant change in sample composition even at longer durations. The sustained mechanical

performance, coupled with the clear presence of brucite and M-S-H even at longer durations, suggested that these phases did not decompose under any of the durability environments. These outcomes could be used to highlight the potential of MgO-SiO₂ formulations to be utilized in structural applications. Further studies on the volume stability and changes in the chemical composition of MgO-SiO₂ samples under other aggressive environments would further increase the knowledge about their long-term durability.

8.2. Future work

The four main areas investigated in this study were the (i) influence of mix design and curing conditions on sample performance and microstructure, (ii) development of M-S-H cements with rice husk ash, (iii) influence of carbonation curing on MgO and MgO-SiO₂ based samples, and (iv) durability and associated performance of MgO-SiO₂ based concrete under various conditions. While the findings emerging from this study led to a significantly improved understanding of MgO-SiO₂ formulations and shed light on their feasibility to be used as a binder in building applications, further studies can be performed to investigate the factors that have not been studied before and to enhance the performance of the developed formulations.

Many of the previous studies in the literature focused on MgO-SiO₂ formulations in the form of pastes, rather than mortar or concrete. Only a few recent studies involved use of fine or coarse aggregates in the mix compositions. The research direction of future studies should be towards the utilization of MgO-SiO₂ formulations in building applications. In order for MgO-SiO₂ formulations to be used in real-life building applications, further work on the performance of MgO-SiO₂ based concrete, which incorporates fine and coarse aggregates, has to be performed. This should involve a thorough comparison of performance and microstructure with corresponding PC-based concrete mixes. Further work on MgO-SiO₂ based concrete should first focus on optimizing the mix composition with the inclusion of fine and coarse aggregates. Subsequently, the introduction of steel reinforcement within MgO-SiO₂ based

formulations should be studied and compared with traditional reinforced concrete samples.

Another aspect that should be studied further is the stability and long-term performance of MgO-SiO₂ based concrete formulations. The results obtained so far have shown that MgO-SiO₂ mixes may experience some cracking when exposed to under water curing for long durations. In line with these findings, the formation and stability of hydration products, M-S-H and brucite, should be addressed, especially under water and at elevated temperatures. The volume stability of MgO-SiO₂ based binders should be examined in detail to identify the mechanism leading to observed cracks. Once the exact mechanism for crack formation is revealed, improvements must be made to prevent their formation and enable the maintenance of sample integrity under these conditions. Further studies in this area should also look into the performance of these samples under elevated temperatures and establish the fire resistance of the developed formulations according to the existing standards.

The findings presented in this study have shown that M-S-H can be effectively obtained by using amorphous RHA as a silica source in MgO-SiO₂ formulations. Further studies on the determination of ideal conditions for the production of fully amorphous RHA and the optimization of mix designs involving its use can further improve the mechanical performance of MgO-SiO₂ formulations. Besides RHA, the use of other waste materials and by-products with high amorphous silica contents in MgO-SiO₂ mixes should be investigated to reduce the overall environmental impacts of the developed formulations. Sugarcane bagasse ash could be one of the promising alternative waste materials with its SiO₂ content reaching as high as 60-70%. Additionally, a detailed life cycle assessment (LCA) should be performed to analyse the environmental impacts of MgO-SiO₂ formulations and provide a comparison with existing binders.

The results on the use of carbonation curing on the strength development of MgO-SiO₂ formulations have shown to be useful in terms of strength and microstructural

development. Further studies can be performed for the optimization of the initial mix design and curing conditions (e.g. CO₂ concentration, relative humidity and temperature) to provide even higher strengths by enabling the complete consumption of MgO in the hydration and subsequent carbonation reactions. This should be accompanied with an investigation of the effect of these parameters on the properties, stability and transformation of the final hydrate and carbonate phases that form under different environments.

The findings presented in this study have shown that the performance of MgO-SiO₂ based concrete was not detrimentally affected upon its exposure to severe conditions including sodium chloride (NaCl), magnesium chloride (MgCl₂) and magnesium sulfate (MgSO₄) environments. Influence of other severe environments such as acid attack, freeze-thaw and seawater on the performance of MgO-SiO₂ based concrete has to be investigated to establish a complete understanding of its durability and provide a comparison with existing PC-based samples. The changes in the performance of these formulations should be accompanied with a detailed microstructural analysis that will reveal the changes in the chemical composition of the formed products.

The obtained results so far have established a pathway towards understanding the performance and durability of MgO-SiO₂ formulations under various conditions. The continuation of this research in the directions listed above will enable the end users within the construction industry to make more informed choices about the properties of these binders that can present an alternative to PC. The results emerging from this study can lead to the development of MgO-SiO₂ binders with lower environmental impacts and comparable mechanical performance to existing binder systems.

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APPENDIX

Appendix – Average and standard deviation (SD) of compressive strength (CS) values for M and P samples in Chapter 7

M Samples (MPa)		CS and (Standard Deviation) of samples under different environmental conditions					
Test Duration	C	CA	W	SC	MC	MSu	
Day 28	76.4 (3.6)	78.3 (12.1)	64.4 (1.5)	69.2 (8.1)	69.1 (2.9)	75.0 (2.8)	
Day 56	79.3 (6.0)	81.4 (8.4)	65.6 (1.8)	68.8 (16.7)	73.9 (21.0)	79.2 (4.9)	
Day 90	84.4 (2.1)	81.2 (0.9)	64.8 (2.1)	72.1 (1.8)	77.3 (1.7)	79.6 (4.0)	
Day 180	83.3 (1.6)	80.7 (4.7)	64.6 (4.2)	71.6 (3.1)	73.6 (0.4)	77.1 (0.9)	
CS and SD at Day 0: 64.9 (8.7)							
CS: Value on the left, Standard deviation: Value in brackets							

P Samples		CS and (Standard Deviation) of samples under different environmental conditions					
(MPa)							
Test		C	CA	W	SC	MC	MSu
Duration							
Day 28		57.4 (2.7)	72.8 (4.6)	55.9 (3.6)	55.4 (4.9)	47.4 (2.6)	52.9 (2.5)
Day 56		60.5 (4.1)	76.4 (2.5)	63.7 (8.9)	61.9 (4.3)	46.4 (2.4)	53.4 (3.3)
Day 90		66.3 (6.6)	82.9 (13.5)	75.7 (11.0)	62.5 (4.4)	44.6 (1.5)	52.1 (4.9)
Day 180		74.0 (6.3)	91.1 (3.8)	80.1 (1.1)	63.1 (2.1)	46.1 (0.3)	53.9 (1.6)
CS and SD at Day 0: 55.2 (3.7)							
CS: Value on the left, Standard deviation: Value in brackets							