Microwave-based Preconditioning for Accelerated Carbonation Curing of Cementitious Materials

A thesis submitted to
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by
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I, Min Liu, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.
Abstract

To increase the manufacturing efficiency of precast concrete, carbonation curing has been increasingly recognised as a potential technique to effectively address the sustainability issues facing construction industry. However, the water demand needed to ensure sufficient workability of vibrated concrete is relatively high compared to that for the compacted concrete, and is undesirable for carbonation curing. Various preconditioning methods have, therefore, been proposed and developed in the literature to remove excessive water in order to facilitate carbonation curing. However, all these preconditioning methods are inefficient and take a much longer time than the actual carbonation curing. To address this issue, a microwave-based method has been successfully developed in this project as an alternative preconditioning technique for accelerated carbonation curing. This has been achieved through a comprehensive study as reported in this thesis.

Firstly, the effects of preconditioning time, carbonation time and carbonation pressure on the properties, reaction products and carbonation efficiency of cementitious materials were systematically studied. It was found that the microwave-based heating is an effective preconditioning method, which can reduce the threshold preconditioning time to around 70 min. A change in carbonation time results in different carbonation products and a higher degree of carbonation, while a change in carbonation pressure leads to little difference in carbonation products. Compared with other preconditioning methods, the microwave-based preconditioning removes water and enhance carbonation rapidly. The reaction products for the microwave-based preconditioning were found to be similar to those for other preconditioning methods. Furthermore, the application of the established microwave-based preconditioning and carbonation curing regime to samples was then extended to include different mineral additions. The mortars containing mineral additions had greater carbonation depths and CO$_2$ uptake when compared to the pure cement mortar.

In general, the microwave-based preconditioning in this project shows a good potential, as a novel and effective preconditioning method, for accelerated
carbonation curing of cementitious materials.
Impact statement

The precast concrete industry has been expanding in recent years. Carbonation curing is being increasingly recognised as a potential technique to improve the manufacturing efficiency and the sustainability of precast concrete. However, the water content that is suitable for the carbonation curing is much lower than that required to ensure sufficient workability of concrete. As a result, preconditioning of concrete products to remove part of the free water in order to facilitate the subsequent carbonation curing process is essential. Various preconditioning methods, such as exposure to low humidity (RH 50%) for 18h or steam curing for several hours, have been reported in the literature. However, these preconditioning methods are inefficient and take a much longer time than the actual carbonation curing. Microwave heating which relies on a volumetric heating mechanism is much faster and more efficient. In this study, a microwave-based preconditioning method has been successfully developed as an alternative to allow accelerated carbonation curing. It is found that microwave-based preconditioning is more efficient than other preconditioning methods with the preconditioning time could be reduced from 24 hours to 70 minutes. It also can be applied to cementitious materials containing various additions so that whilst the carbon footprint can be reduced without affecting the early-age properties of concrete. It is anticipated that this microwaved-based preconditioning method will eventually enable the concrete cast by vibration to be efficiently cured by carbonation curing technique due to the fact that extra free water added in the compacted concrete for workability purpose can be effectively removed by microwave-based preconditioning.

This study has both academic and societal impacts. Firstly, it provides a deeper understanding of the mechanism involved in the microwave-based preconditioning technique, benefiting the future wider industrial applications. Secondly, combining microwave-based preconditioning with accelerated carbonation curing techniques, which can be potentially applied to precast concrete, can increase the early strength of concrete, in particular, low-carbon concretes, whilst the CO₂ also can be effectively absorbed by concrete during the same time. Additionally, by combining the microwave-based preconditioning
and the carbonation curing techniques, the curing duration can be reduced from around 24 hours down to 4h, which can effectively increase the productivity and, at the same time, reduce the cost. Overall, the outcome from this research project can not only benefit the UK and other countries to meet the targets set for reducing the CO$_2$ emissions. but will also benefit the human society in building a sustainable world in the future.
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List of Abbreviations

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<th>Term</th>
<th>Explanation</th>
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<tbody>
<tr>
<td>CH</td>
<td>Ca(OH)$_2$</td>
</tr>
<tr>
<td>PC</td>
<td>Portland cement</td>
</tr>
<tr>
<td>FLY ASH</td>
<td>Pulverised fuel ash</td>
</tr>
<tr>
<td>GGBS</td>
<td>Granulated blastfurnace slag</td>
</tr>
<tr>
<td>AFT</td>
<td>Ettringite</td>
</tr>
<tr>
<td>Ca/Si ratio</td>
<td>Calcium/silicate ratio</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>DEF</td>
<td>Delayed ettringite formation</td>
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Chapter 1  
Introduction

1.1  Research background

1.1.1  Introduction

Global climate change has been attracting much attention in recent decades. The Intergovernmental Panel on Climate Change (IPCC, 2018) has reported that the global temperature has risen by 0.85°C, and the sea level has raised by 0.19 metres. Additionally, the frequency of extreme climate events has greatly increased since the beginning of the industrial era. These are highly likely due to the increase in the concentration of CO$_2$ in the atmosphere over the same period (IPCC, 2018).

Concrete is the most widely used man-made material in the world. The manufacture of the main component of concrete, Portland cement (PC) alone, is reported to account for around 5% of global CO$_2$ emissions (Fonta, 2013). Therefore, any reduction in the CO$_2$ emissions related to the use of concrete could significantly contribute to a reduction in the global CO$_2$ emissions.

The replacement of cement with mineral additions in concrete represents a good approach for decreasing CO$_2$ emissions. Such additions include fly ash, limestone powder, granulated blast furnace slag (GGBS) (Neville, 2011). Fly ash is the residual ash from the precipitation of dusts from the burning of coal in power plant; GGBS is the waste produced by the rapid cooling of the smelting slag in blast furnace; limestone powder can be obtained from natural sources and is a waste material from aggregate crushing operation and other industries (Bentz et al., 2017).

These additions are normally stockpiled at particular locations, which is detrimental to the environment. Their replacements of cement in concrete can, however, be both beneficial to the environment and reduce the CO$_2$ emissions. Based on BS 197-1:2000, it is prescribed that the upper limit of the replacement ratio of cement with limestone, fly ash and GGBS can be 35% (in CEM II).
While fly ash and GGBS are considered as two typical supplementary materials, which can react with calcium hydroxide and develop later strength, limestone powder is generally regarded as an inert material at early age though it can react with calcium aluminates in the long run (Neville, 2011). Overall, however, these three additions can result in a severe reduction in the early strength of the concrete (Moon et al., 2017, Thongsanitgarn et al., 2014, Soutsos et al., 2017). As a result, accelerated curing methods are needed to enhance the early strength of concrete containing these additions.

1.1.2 Accelerated curing

Steam curing is the most commonly used technique in precast concrete, especially that containing additions, to enhance the early strength of the concrete (Aqel and Panesar, 2016, Mei et al., 2018, Wu et al., 2017). This method refers to placing the concrete into an enclosed environment with moisture and an elevated temperature, to accelerate the hydration of the concrete. A typical operation cycle is shown in Figure 1.1 (Ong and Akbarnezhad, 2015). Steam curing normally starts with a 3-5 hour delay time before the temperature is increased; the delay time is designed to allow the concrete to develop sufficient early strength. A higher early strength can withstand the tensile stress generated during the subsequent heating (Erdem et al., 2003). After the temperature is increased, it is maintained at a certain level for 10 to 18 hours (Won et al., 2015). In total, one operation cycle of the steam curing process could last for 24 hours (Makul et al., 2010).
Despite the advantages of steam curing in enhancing the early strength, the process is relatively long. In addition, this process is also criticized because of its high energy consumption (estimated to be 0.59 GJ per m$^3$ of concrete) (El-Hassan and Shao, 2014a), which could offset the reduction of the carbon footprint gained by using the additions.

Carbonation curing is a recent hot topic among researchers and it refers to exposing the concrete to CO$_2$ at an early stage of the hydration, usually within the first 24h (Zhu et al., 2018, Zhang and Panesar, 2018b, Zhang and Panesar, 2018a, Tu et al., 2018). Normally, concrete is placed in a chamber with a high concentration of CO$_2$, 20% or even 100%, and at pressures equal to or greater than atmospheric pressure (Malinowski, 1985, Ramme et al., 2008, Zhang and Shao, 2016a). This differs from normal carbonation in which the sample is only subjected to atmospheric CO$_2$ concentration (0.04% concentration).

The literature suggests that carbonation curing rapidly consumes calcium silicates and produces a CaCO$_3$ and C-S-H gel with low Ca/Si ratio, which are both sources of strength (Shao et al., 2014, Morshed and Shao, 2014, Rostami et al., 2012b, Shi et al., 2012a). Carbonation curing usually lasts less than 2 hours and yields a noticeable strength gain; this indicates the possibility of
using carbonation curing to promote the efficiency of curing. In addition, the carbonation curing process absorbs a high percentage of the CO$_2$ rather than emitting CO$_2$ as occurred in the steam curing process, thus making carbonation curing a much more eco-friendly curing method. Furthermore, the concrete after carbonation curing has been reported to have a better performance in terms of chloride penetration and sorptivity (Rostami et al., 2011), better sulphate and acid resistance (Rostami et al., 2011), and lower drying shrinkage (Shi et al., 2012b).

However, despite the advantages brought about by carbonation curing, there is an issue that limits the application of CO$_2$ curing technology. In order to obtain a high degree of carbonation, a limited water content (w/c ratio of 0.15) is needed to ensure the interaction between CO$_2$ and the cementitious particles (Berger and Klemm, 1972, Monkman et al., 2009, Mu et al., 2018). For the vibrated concrete, the w/c ratio is much higher (0.3 ~ 0.7) (Neville, 2011). With an excessive water, CO$_2$ cannot interact effectively with the cement particles, and thus reduces the degree of carbonation (Klemm and Berger, 1972). To satisfy a good workability of the vibrated concrete, higher w/c ratio has to be adopted. As a result, preconditioning is required prior to carbonation curing to reduce the water content in order to facilitate carbonation curing.

### 1.1.3 Preconditioning methods prior to carbonation curing

In order that carbonation curing can be used in normally vibrated concrete, preconditioning is needed to bring the water content down to the right level before the carbonation takes place (Shi et al., 2012a, Morshed and Shao, 2014, El-Hassan and Shao, 2014b). The usual methods for preconditioning include exposure to an environment with a lower relative humidity and steam curing (Rostami et al., 2011, Sharma and Goyal, 2018, Zhang and Shao, 2016a). However, these preconditioning methods take a long time, usually between 4 to 18 hours (Shi et al., 2012a, Morshed and Shao, 2014, El-Hassan and Shao, 2014b), to reach the optimum carbonation efficiency; however, the carbonation curing itself normally takes 2 hours. In this case, carbonation curing is no longer desirable as the whole process takes a long time. Therefore, there is a need to
develop a fast and efficient preconditioning method in order to take the full advantages of carbonation curing.

Microwave heating, which has already been widely used in the food drying and timber drying industries (Guo et al., 2017, Bal et al., 2017, Zhang et al., 2006), is proposed as a promising preconditioning method in this project. Microwave heating relies on volumetric heating to heat and dry samples, and is time saving (Makul et al., 2014). The microwave field induces vibration and friction of dipolar molecules inside samples, thus converting the microwave energy into volumetric heating in the samples (Loupy, 2002). The microwave drying method has been reported to be more efficient compared with the conventional heating methods (Soysal, 2004). The more efficient drying is attributed to its unique mechanism of heating that accelerates the migration of moisture from the internal to the surface of samples (Zielonka and Dolowy, 1998, Li et al., 2018a, Mujumdar, 2006). Therefore, microwave heating can be potentially used as an efficient preconditioning method, which is expected to greatly reduce the preconditioning time to reach the optimum water content for carbonation curing.

Therefore, the research question raised in this project is: **Is microwave heating an efficient preconditioning method to increase carbonation efficiency? If so, how should this combined microwave heating and carbonation curing methods be applied to cementitious materials?**

### 1.2 Aim and objectives

The primary aim of this project is to develop a microwave-based preconditioning method which can enable the carbonation curing to be applied to the normally vibrated concrete in order to effectively improve its early strength and reduce CO$_2$ emissions. To achieve this aim, the following objectives were identified:

1. To investigate the factors that affect the microwave-based preconditioning and carbonation curing regime when applied to a normally vibrated mortar, with the intention of developing a suitable preconditioning and carbonation regime;
(2) To identify the effectiveness of microwave heating as a preconditioning method to facilitate carbonation curing by comparing the efficiency of microwave heating with other preconditioning methods reported in the literature;

(3) To determine the effectiveness of microwave-based preconditioning for carbonation curing the cement paste and mortar containing different mineral additions;

1.3 Outline of the thesis

Chapter 1 describes the overview of the project.

Chapter 2 reviews the process, mechanism, and the factors affecting carbonation curing. In this chapter, the current problems of using the existing preconditioning methods are, in particular, being identified.

Chapter 3 reviews the principle of microwave heating and its application to cementitious materials as well as its role as a drying technique. From this, the utilization of microwave heating as an alternative preconditioning method is proposed.

Chapter 4 then describes the methodology and experimental programme developed and adopted for this project.

Chapter 5 investigates the effects of microwaving time, CO$_2$ pressure and carbonation time on the properties, microstructure and reaction products of cement paste and mortar, with an aim to develop an optimized preconditioning and carbonation regime.

Chapter 6 compares the preconditioning efficiency of microwave heating with other preconditioning methods reported in the literature.
Chapter 7 studies the efficiency of microwave-based preconditioning for carbonation curing of cement pastes and mortars containing different mineral additions including fly ash, GGBS and limestone powder, and finally,

Chapter 8 draws the main conclusions and makes some recommendations for future work.
Chapter 2 Accelerated carbonation curing for cementitious materials

2.1 Introduction

To increase the manufacturing efficiency of precast concrete products, accelerated curing, such as steam curing, is widely used to accelerate the hydration of cement and, thus, to improve the early-age compressive strength of concrete (Mei et al., 2018, Long et al., 2017, Hanif et al., 2017, Gonzalez-Corominas et al., 2016, Yazıcı et al., 2005). However, steam curing is not only energy-extensive, but also time-consuming. In recent years, carbonation curing has been increasingly recognised as a potential technique to address the above issues facing the precast concrete industry (Zhang and Panesar, 2018b, Zhang and Panesar, 2018a, Tu et al., 2018, Sharma and Goyal, 2018, Seo et al., 2018a).

This chapter reviews the process and mechanisms of carbonation curing on cement. Then the effects of carbonation curing on properties of cementitious materials and the factors affecting the carbonation curing are discussed and summarized. Finally, the preconditioning methods for carbonation curing are highlighted and discussed.

2.2 Process of carbonation curing

Carbonation curing refers to exposing cementitious materials to CO₂ (100% concentration) at pressures between 1 bar and 5 bar at an early stage with the intention of increasing their strengths and CO₂ uptake (Sharma and Goyal, 2018, Mu et al., 2018, Zhang and Shao, 2018). In contrast, if the matured concrete is subjected to CO₂ with a low concentration (normally below 20%), this is called weathering carbonation (Neville, 2011). In the weathering carbonation process, due to the gradual carbonation of matured concrete, the pH inside the concrete drops and induces the corrosion of steel reinforcement. So weathering carbonation is considered as a durability issue in practice (Talakokula et al., 2016, Silva et al., 2015, Köliö et al., 2015). The detailed
differences between the carbonation curing and weathering carbonation are introduced in Section 2.4.7. In this project, carbonation curing that deliberately exposes the concrete to CO$_2$ at an early stage is studied.

As the carbonation curing process starts at an early stage, the carbonation of unreacted calcium silicates is the primary reaction. This section will use C$_3$S as an example to illustrate the process of carbonation curing (Fernandez Bertos et al., 2004, Visser, 2014). The sample refers to the C$_3$S paste sample moulded by compaction and subjected to carbonation immediately.

**Step 1: Transport of gaseous CO$_2$ into samples.** There are several factors directly affecting the transport of the gas, including: 1) the water content in the C$_3$S paste; 2) the permeability of the sample; and 3) the partial pressure of CO$_2$. Among these factors, the water content is a critical factor because the gaseous CO$_2$ diffuses 4 orders of magnitude slower in water than that in air (Neville, 2011). A lower water content results in a higher rate of transport of CO$_2$. Secondly, the permeability of the sample is also an important factor, which is determined by the sample’s inherent properties, such as the porosity and the connectivity of the pores. Thirdly, the partial pressure of the CO$_2$ is also an influencing factor. As pressurized CO$_2$ is often used in the carbonation curing process, it would cause concentration gradients and pressure gradients (Phung et al., 2015, Zou et al., 2015). This will be further explained in Section 2.5.6.

**Step 2: Dissolution of gaseous CO$_2$ in liquid.** The amount of CO$_2$ that dissolves in solution equilibrates with the gaseous CO$_2$ in the air, and it is proportional to the partial pressure of the CO$_2$. The dissolution of CO$_2$ is shown in (Eq 2.1). The concentration of CO$_2$ dissolved in the pore solution can be calculated from Henry’s law, with Henri’s constant being determined at a specific pressure and temperature (Carroll et al., 1991). This will be further explained in Section 2.5.6. A higher CO$_2$ pressure leads to a higher concentration of dissolved CO$_2$.

\[
CO_2(g) ⇌ CO_2(l) \tag{2.1}
\]
Step 3: Hydration and ionization of CO$_2$ (l). After CO$_2$ has dissolved in water, both CO$_3^{2-}$ and HCO$_3^-$ ions are produced. Eqs 2.2, 2.3 and 2.4 show the sequence of the hydration and ionization of CO$_2$ (Visser, 2014). It can be seen from these equations that the concentrations of CO$_3^{2-}$, HCO$_3^-$, and H$^+$ ions are dependent on the partial pressure of the CO$_2$, as seen in step 2.

$$CO_2(l) + H_2O \rightleftharpoons H_2CO_3$$ \hspace{1cm} (2.2)

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$ \hspace{1cm} (2.3)

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$ \hspace{1cm} (2.4)

The formation of H$^+$ results in a reduction in pH. Table 2.1 shows typical pH values varying in pure water with partial pressure of CO$_2$ based on calculation (Visser, 2014). Higher partial pressure leads to a drop in pH, but after the partial pressure exceeds 1 bar, there is little change in pH value.

<table>
<thead>
<tr>
<th>P$_{CO_2}$ (bar)</th>
<th>3.5×10$^{-4}$</th>
<th>1</th>
<th>2.5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.65</td>
<td>3.92</td>
<td>3.72</td>
<td>3.42</td>
</tr>
</tbody>
</table>

Step 4: Dissolution of C$_3$S in water. This step occurs at the same time as steps 1, 2, and 3 and it is a dissolution process, which produces Ca$^{2+}$ and OH$^-$ ions. If the samples are exposed to carbonation immediately, the produced ions would take a longer time to precipitate (Scrivener and Nonat, 2011).

$$C_3S + H_2O \rightleftharpoons Ca^{2+} + OH^- + SiO_4^{2-}$$ \hspace{1cm} (2.5)

If the samples are not exposed to carbonation immediately, the produced ions would precipitate and produce CH and C-S-H gel (Juilland et al., 2010).

$$Ca^{2+} + OH^- + SiO_4^{2-} \rightleftharpoons Ca(OH)_2 + C - S - H$$ \hspace{1cm} (2.6)

Step 5: Consumption of Ca$^{2+}$ and OH$^-$ (Eq 2.7 and 2.8) if there are no precipitates of CH and C-S-H gel. Eq 2.7 is a precipitation process and the
reaction continues as long as there are \( Ca^{2+} \) and \( OH^- \) ions present. The precipitation reactions promote Step 4. The details of the acceleration of hydration will be discussed in Section 2.3.

\[
CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3 \tag{2.7}
\]

\[
OH^- + H^+ \leftrightarrow H_2O \tag{2.8}
\]

The \( H^+ \) ions produced from step 3 are consumed by the hydration product of the C_3S, and this reduces the rate of decrease in the pH. Only after the dissolution of C_3S stops will the pH start to decrease. The remaining \( SiO_4^{2-} \) reacts with \( Ca^{2+} \) and they precipitate as C-S-H gel (Berger et al., 1972).

Step 6: Consumption of \( Ca^{2+} \) and \( OH^- \) if there are precipitates of CH and C-S-H gel. With the exposure to CO_2, CH quickly dissolves in water to produce \( Ca^{2+} \) and \( OH^- \), and then follow as step 4. At the same time, the conventional C-S-H gel dissolves and produces \( Ca^{2+} \), which reacts with \( CO_3^{2-} \) to form precipitate and a lower Ca/Si ratio C-S-H gel. Eq 2.9 shows that \( CO_3^{2-} \) reacts with a relatively high Ca/Si ratio C-S-H gel (Ca/Si 1.5) to form a relatively low Ca/Si ratio C-S-H gel (Ca/Si ratio 0.2 ~ 1.4) (Berger et al., 1972).

\[
C_xSH_y + CO_3^{2-} \rightarrow C_x'SH_y' + CaCO_3 + H_2O; x > x' \tag{2.9}
\]

From what has been discussed so far, the \( Ca^{2+} \) produced by the dissolution of C_3S can react rapidly with \( CO_3^{2-} \) from the dissolved gaseous CO_2 (step 5); the reaction is so rapid that it can even be assumed to be instantaneous (Visser, 2014). This rapid reaction is considered to be the main reason that the reactions of steps 2, 3, 4 are promoted. In fact, the reactions of steps 2, 3, and 4 are also very rapid (Visser, 2014). However, without sufficient supply of CO_2, none of the above reactions could be sustained or even triggered. Therefore, step 1 (the transport of CO_2) is considered as the most important factor that influences the entire reactions.
Hence, all the factors that can influence the rate of transport (i.e. Step 1) must be fully understood and carefully considered in the carbonation curing process. Therefore, the effect of some typical factors, such as degree of hydration, water/cement ratio, relative humidity, CO₂ pressure and carbonation time, on the transport of carbonation are further reviewed and discussed in Section 2.5 below.

2.3 Mechanism of carbonation curing

This section mainly discusses how carbonation curing promotes the hydration of Portland cement (PC) (i.e. how Step 5 affects Step 4). As the process of hydration has been extensively studied, the mechanism of the hydration of C₃S is briefly explained and then the effect of carbonation curing on the hydration is discussed.

2.3.1 Mechanism of hydration of C₃S/alite

C₃S/Alite is the main component of PC, which accounts for up to 70% of the cement. A good understanding on the hydration of C₃S is, therefore, the key to the understanding of the mechanism of PC hydration. Figure 2.1 shows a typical heat flow together with the amount of calcium released during the hydration of alite (Juillard et al., 2010). In the figure, the Period I represents the rapid dissolution of the anhydrous phase accompanied by an increase in the calcium concentration, whilst the Period II shows the low rate of reactivity which is known as the induction period. Period III is an acceleration period after the induction period. Finally, a decreasing rate of reaction occurs in Period IV.
When C₃S first encounters water, the rate of dissolution is high and \(Ca^{2+}, OH^-\) and \(SiO_2^{2-}\) are quickly produced. Based on the dissolution theory (Juilland et al., 2010, Nicoleau et al., 2013), this is caused by the relatively large difference between the solubility and ion activity of C₃S in solution. Then the rate of dissolution decreases as concentrations of ions remain at high levels at which point the induction period occurs. This is caused by the relatively small difference between the solubility and ion activity of C₃S in solution. Once the amount of ions in solution increase to a certain level, the ions precipitate as both CH and C-S-H gel. The precipitations of CH and C-S-H gel result in a loss of ions in the solution and increase the difference between the solubility and ion activity of C₃S in solution, causing the initiation of the acceleration stage. However, the induction period does not appear in the carbonation curing process (Berger et al., 1972, Li et al., 2018b).

### 2.3.2 Mechanism of carbonation curing of C₃S, C₂S and C₃A

As discussed before, the dissolution theory considers the difference between the solubility and ion activity of C₃S in solution as the driving force for dissolution (Juilland et al., 2010, Nicoleau et al., 2013). The precipitation of CH and C-S-H gel decease the ions of \(Ca^{2+}, OH^-\) and \(SiO_2^{2-}\) that terminates the
induction period. However, with carbonation curing, the consumption of the former two ions can be even quicker due to the formation of CaCO$_3$ and H$_2$O, as seen in Section 2.2. As a consequence, the induction period does not appear during the carbonation curing (Berger et al., 1972, Li et al., 2018b), and the rapid reaction continues and then jumps directly to the acceleration stage. In this case, the consumption of C$_3$S has been greatly accelerated. Similarly, the consumption of C$_2$S has also been speeded up, as seen in the literature (Young et al., 1974, Mota et al., 2015).

As reported (Berger et al., 1972), the reaction equations for the carbonation of C$_3$S and β-C$_2$S are as follows:

\[
\begin{align*}
C_3S + (3 - x)CO_2 + yH_2O &\rightarrow xCaO.SiO_2.yH_2O + (3 - x)CaCO_3 \quad (2.10) \\
C_2S + (2 - x)CO_2 + yH_2O &\rightarrow xCaO.SiO_2.yH_2O + (2 - x)CaCO_3 \quad (2.11)
\end{align*}
\]

These equations suggest that, the consumption of C$_3$S and C$_2$S produces CaCO$_3$ and C-S-H gel, which are both cementing materials and contribute to strength.

C$_3$A is also an independent component of PC, and its reaction during the carbonation curing is also of interest. However, as far as the author’s knowledge, there is little study on the carbonation curing of the C$_3$A yet.

### 2.3.3 Mechanism of the carbonation curing of cement

Cement is a complex material containing four main compounds, C$_3$S, C$_2$S, C$_3$A and C$_4$AF. In addition, gypsum is interground with clinker. Without the presence of gypsum, the C$_3$A quickly dissolves into solution, and would lead to flash setting. With the addition of gypsum, the dissolution of C$_3$A slows down because of the adsorption of $SO_4^{2-}$ from the dissolution of gypsum (Minard et al., 2007). The C$_3$S and β-C$_2$S hydrate normally not being strongly influenced by C$_3$A.
After the introduction of CO$_2$, the $CO_3^{2-}$ and $HCO_3^-$ in this solution react with the Ca$^{2+}$ released by the CaSO$_4$ to form $SO_4^{2-}$ and CaCO$_3$, as CaCO$_3$ has a lower solubility than CaSO$_4$ (Azdarpour et al., 2014). Consequently, the $SO_4^{2-}$ remains in the solution, impeding further dissolution of C$_3$A and preventing flash setting (Minard et al., 2007). In the meantime, as discussed earlier, there is a very rapid acceleration in the hydration of C$_3$S and $\beta$-C$_2$S. The reaction continues until the CaCO$_3$ that forms on the surface of cement grains impedes further reaction.

Ettringite is a common hydration product from the reaction between C$_3$A and CaSO$_4$. It is reported to decompose at a pH lower than 10.6, and forms calcium carbonate, alumina gel, gypsum and water (Nishikawa et al., 1992, Visser, 2014), but the pH on the surface of the concrete sample after carbonation curing is only 9.2 ~ 9.4 (Shi and Wu, 2008, Zhang and Shao, 2016b). Therefore, ettringite is not expected when the samples are subjected to carbonation curing.

After carbonation curing, the unreacted C$_3$A reacts with the produced CaCO$_3$ and gradually form C$_3$A·CaCO$_3$·11H$_2$O over time (Kuzel and Pöllmann, 1991, Kakali et al., 2000). The phase C$_3$A·CaCO$_3$·11H$_2$O has been detected at 7d, 28d and 90d hydration after carbonation curing (He et al., 2016).
2.4 Effects of carbonation curing on properties of cementitious materials

From the discussion in Section 2.3, it can be concluded that carbonation curing of cement can effectively promote the hydration rate. Equations 2.10 and 2.11 show that the carbonation curing of C₃S and C₂S creates C-S-H gel as well as CaCO₃. The C₃A reaction is not affected by carbonation curing, although the CaCO₃ may react with the C₃A in the long run to form C₃A·CaCO₃·11H₂O.

Carbonation curing results in combined physical and chemical effects on the cementitious materials. For example, the promoted hydration rapidly increases the generation of C-S-H gel and CaCO₃ (chemical effect) (Mo et al., 2017, Tu et al., 2016, Zhang and Panesar, 2018b), thus reducing the porosity (physical effect) (He et al., 2016, Neves Junior et al., 2015). The rapid promotion of hydration causes a rapid temperature increase in the samples (physical effect) (Shi et al., 2012a, Shi et al., 2012b, Monkman and Shao, 2006). The combined physical and chemical effects influence the development of the strength (Shi et al., 2012b, Monkman and Shao, 2006) and durability of cementitious materials (Zhang and Shao, 2016a, Neves Junior et al., 2015).

This section reviews the effects of carbonation curing on the rate of reaction, the properties of cementitious materials such as strength and porosity, and their carbon footprints, and compares these with the effects of natural carbonation.

2.4.1 Effects on the reaction rate of C₃S and C₂S

As seen in Section 2.3, the carbonation reaction can increase the rates of hydration of C₃S and C₂S. From the much higher strength achieved and qualitative X-ray Diffraction (XRD), it can be determined that a reasonable amount of C₃S and C₂S have been consumed during the carbonation of cement (Monkman and Shao, 2006, Mo et al., 2017, Tu et al., 2016, Zhang and Panesar, 2018b).
In addition, the rate of consumption of $C_2S$ in normal hydration is much slower than that for $C_3S$, but their rates of consumption are comparable when carbonation curing is applied. It was reported by Young et al. (1974) that after only 27 minutes of carbonation curing, the consumption of $C_3S$ could reach approximately 30%. A similar degree of reactivity was found for $\beta$-$C_2S$ (Goodbrake et al., 1979). Tu et al. (2016) showed that after 24h carbonation of cement, the percentages of $C_3S$ and $\beta$-$C_2S$ reduced from around 48% and 26% to 13% and 9%, respectively.

In summary, the rate of the consumption of calcium silicates is much higher with carbonation curing of cement than conventional hydration. As discussed in Section 2.3, the consumption of calcium silicates is generally accompanied by the production of CaCO$_3$ and C-S-H gel, which can improve the compressive strength.

### 2.4.2 Effects on temperature rise and accompanying water evaporation

Carbonation curing significantly accelerates the chemical reaction which is accompanied by the release of a large amount of heat in a short time (Goodbrake et al., 1979, Li et al., 2018b, Monkman and Shao, 2006). The release of the heat is rapid and tremendous.

Li et al. (2018b) showed that the $C_3S$ paste released heat which reached the peak in just few minutes. The studies by Lange et al. (1996) and Shi (2012b) confirmed that the highest CO$_2$ consumption took place during the first 20 minutes. Shi et al. (2012a) monitored the temperature changes of a lightweight concrete at different depths during the carbonation curing (Figure 2.2). Results showed that both surface and inside layers reached the peak temperature during the first 20 minutes, after which the temperature decreased to ambient temperature. It also shows a higher temperature occurred in the surface layer than the inside layer, indicating a higher degree of carbonation in the surface of the samples. A study by Monkman and Shao (2006) showed that the temperature of the surface of a compacted cement paste sample (w/c ratio 0.15) could reach as high as 130°C.
This high temperature leads to water evaporation during the carbonation curing process (Young et al., 1974). The water that evaporates during the carbonation curing was reported to be 26% of the original water (Monkman and Shao, 2006). As a consequence, the remaining water is then inadequate for future hydration.

**2.4.3 Effects on pore structure**

Pore structure is an important parameter that affects the strength of concrete, with a refined pore structure generally increasing the strength of the concrete (Neville, 2011). In this context, it is important to note that carbonation curing can decrease the porosity of cementitious materials. The main reason can be attributed to the rapid formation of CaCO$_3$ and C-S-H gel when CO$_2$ reacts with calcium silicates at an early stage of the carbonation curing. This reaction is a volumetric increase process and thus refines the pore structure.

Zhang and Shao (Zhang and Shao, 2018) studied the pore structure of PC mortar before and after carbonation, and found that the pore volume decreased by 40% after carbonation and the critical diameter reduced from 50 nm to below 10 nm. Lu et al. (Lu et al., 2018) compared the pore structure of non-carbonated and carbonated low-calcium clinker, and observed that the porosity
decreased and also the threshold diameter decreased from 0.08 μm to 0.04 μm. Similar phenomenon have also been found in the studies of (He et al., 2016, Neves Junior et al., 2015).

In summary, carbonation curing has been proved to reduce porosity and refine the pore structure, which can contribute to a higher strength and better durability.

### 2.4.4 Effects on strength development

As discussed above, carbonation curing produces more CaCO$_3$ and C-S-H gel together with a refined pore structure which can significantly improve the compressive strength. The compressive strength of samples with appropriate water content (w/c ratio 0.125 ~ 0.15) after carbonation are shown in Table 2.2.

<table>
<thead>
<tr>
<th>Materials</th>
<th>W/B ratio</th>
<th>Sample size (mm)</th>
<th>Carbonation duration</th>
<th>Compressive strength after carbonation (MPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$S mortar</td>
<td>0.125</td>
<td>Ø15.9×19</td>
<td>81 min</td>
<td>70</td>
<td>(Young et al., 1974)</td>
</tr>
<tr>
<td>(s/c = 1:1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-C$_2$S mortar</td>
<td>0.125</td>
<td>Ø15.9×19</td>
<td>81 min</td>
<td>52.7</td>
<td>(Li et al., 2018b)</td>
</tr>
<tr>
<td>(s/c=1:1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_3$S paste</td>
<td>0.15</td>
<td>Ø20×40</td>
<td>24h</td>
<td>62.9</td>
<td>(Monkman and Shao, 2006)</td>
</tr>
<tr>
<td>Cement</td>
<td>0.15</td>
<td>76×127</td>
<td>2h</td>
<td>56.8</td>
<td></td>
</tr>
</tbody>
</table>
It should be noted that in these studies, as the w/c ratio is low, compaction is used to cast the samples, and the compressive strength without carbonation is low (i.e. 24h hydration achieved a strength of 8.6 MPa (Li et al., 2018b), whilst the strengths of the rest samples are barely measurable). The specimens were subjected to carbonation curing immediately and then cast and demoulded, with the compressive strengths after carbonation achieved between 52.7 MPa and 70 MPa.

Despite the fact that the carbonation curing process can improve the compressive strength, excessive water may prevent the access of CO$_2$ to cement minerals. As the concrete normally has a higher water/cement ratio (0.3 ~ 0.6) to ensure the workability of concrete (Neville, 2011) than that required for carbonation curing (0.15), then preconditioning should be used for the concrete to get rid of excessive water prior to carbonation curing, further details of which will be given in Section 2.6.

Overall, carbonation curing can bring out a rapid strength development in a short period of time, which can be an unique advantage of carbonation curing.

### 2.4.5 Effects on CO$_2$ uptake

As can be seen from Eqs 2.10 and 2.11, carbonation curing is a process that consumes CO$_2$, so the curing method can be considered as a CO$_2$ sequestration process. The CO$_2$ uptake is defined as the mass ratio of CO$_2$ absorbed to cement in the samples (Monkman and Shao, 2006). The maximum CO$_2$ uptake for cement can be estimated based on the composition of the cement according to Equation (2.12) (Steinour, 1959). For most cement compositions, the maximum CO$_2$ uptake is about 50%.

\[
CO_2 \text{ (wt\%)} = 0.785 (CaO - 0.7SO_3) + 1.09MgO + 1.42Na_2O + 0.935K_2O \quad (2.12)
\]

However, CO$_2$ uptake cannot achieve its maximum value due to the limit of carbonation time. Based on the literatures (Moon and Choi, 2018, Ahmad et al.,
2017, Zhang and Shao, 2016a, Zhang et al., 2016, Tu et al., 2016, Shi et al., 2012a, El-Hassan and Shao, 2014b), the CO₂ uptake achieved in literature is 4% ~ 17.5%.

2.4.6 Effects on durability

Durability is a critical parameter that determines whether a material can be used in certain exposure conditions by a given industry. The carbonation of cementitious materials results in changes to both the physical properties and the chemical compositions of the concrete, so that its durability is of interest.

For concrete products manufactured with carbonation curing, the biggest concern is the resistance of the reinforcement steel to corrosion caused by the reduced pH within the cover zone of concrete. The passivation film of the reinforcement steel remains in passive state in the pore solution of concrete and could be destroyed when the pH drops to 11 (Talakokula et al., 2016). This, however, does not appear to be of a great issue. Zhang and Shao (2016a) studied fly ash concrete (100 mm cube) subjected to carbonation curing for 12h. The study confirmed that the pH was 13 initially, but reduced to below 10 and 12 in the outer 0-20 mm and in the outer 20-30 mm. However, the pH was almost unaffected in the core. If the steel is located in the centre of the concrete, the formation of a passive film would not be affected. The research conducted by Rostami et al. (2011) observed a better sulphate resistance in samples after carbonation curing (Rostami et al., 2011). This is because the CH produced in the hydration of cement in the presence of excess sulphates, normally reacts with AFm which leads to the formation of AFt (ettringite) and is disruptive (Taylor et al., 2001). However, the carbonation curing process consumes CH that reduces Ca²⁺ availability and prevents such reactions (Rostami et al., 2011).

As the pore structure is greatly refined after carbonation curing, carbonated products have a lower permeability compared with the non-carbonated products (Pan et al., 2017). In addition, the refined pores are less accessible to water and lead to a reduced melting point for ice to enter the pores, therefore, the freeze-thaw ability has been reported to be increased after carbonation curing.
(Neves Junior et al., 2015). Performance in terms of drying shrinkage was also compared for the same exposure duration, and the concrete generated by carbonation curing was found to have a lower shrinkage (Shi et al., 2012b).

In summary, carbonated concrete can have a greater, or at least a comparable, durability compared to non-carbonated counterparts.

2.4.7 Comparison of carbonation curing to normal carbonation

Carbonation curing is a relatively new concept compared to normal carbonation (or weathering carbonation). While the former is a curing method that can be used to enhance the early strength of concrete, the latter has been considered as a durability issue for structural concretes (Talakokula et al., 2016, Köliö et al., 2015). When concrete is used in service, it could be subjected to CO$_2$ attack at atmospheric levels. Since CH is the main hydration product of cement that contributes to the high pH of concrete, its reaction with CO$_2$ reduces the pH of the concrete which then destroys the passive layer of the steel embedded in concrete, leading to the corrosion of steel in reinforced concrete (Neville, 2011). This corrosion is a volume expansive process which can result in the formation of cracks in concrete (Talakokula et al., 2016, Köliö et al., 2015). The difference of carbonation curing and normal carbonation are further summarized in Table 2.3.
Table 2.3 Summary of carbonation curing and normal carbonation

<table>
<thead>
<tr>
<th></th>
<th>Carbonation curing</th>
<th>Normal carbonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting time</td>
<td>Within 24 hours</td>
<td>After months or years</td>
</tr>
<tr>
<td>Carbonation phases</td>
<td>$C_3S$, $C_2S$</td>
<td>$Ca(OH)_2$, $C$-$S$-$H$ gel</td>
</tr>
<tr>
<td>Carbonation duration</td>
<td>Hours</td>
<td>Days or even years</td>
</tr>
<tr>
<td>Carbonation conditions</td>
<td>partial pressure between 1 bar and 5 bar</td>
<td>$CO_2$ concentration usually less than a few %</td>
</tr>
<tr>
<td>Strength</td>
<td>Significantly improved strength ($&gt;700%$)</td>
<td>Strength gain ($&lt;50%$ increase)</td>
</tr>
</tbody>
</table>

As can be seen from Table 2.3, the key difference between these two processes lies firstly in the time when the carbonation starts. In the case of carbonation curing, the reaction starts at the very early ages, at which time the $C_3S$ and $C_2S$ inside the samples undergo a low degree of hydration, and the rate of consumption of $C_3S$ and $C_2S$ can be greatly increased by the carbonation process (Monkman and Shao, 2006, Mo et al., 2017, Tu et al., 2016, Zhang and Panesar, 2018b). As discussed before, these reactions significantly increase the compressive strength by forming gels ($CaCO_3$ and $C$-$S$-$H$ gel) and refining the pore structure (Zhang and Shao, 2018, Lu et al., 2018). In contrast, in normal carbonation, most of the $C_3S$ and a certain amount of $\beta$-$C_2S$ have already been transformed into $CH$ and $C$-$S$-$H$ gel after 28 days, both of which then become the main target phases for carbonation. The strength has been improved as well (Chang et al., 2003, Jerga, 2004, Xiao et al., 2002), due to the conversion of $CH$ to $CaCO_3$ that causes a reduced porosity. Hence compared with the compressive strengths before and after carbonation, normal
carbonation increased < 50% strength of concrete specimens within months (Chang et al., 2003, Jerga, 2004)), but carbonation curing contributed to over 700% increase in the strength of concrete in just hours (Li et al., 2018b, Monkman and Shao, 2006).

Another point of difference between the two processes relates to the carbonation conditions. For normal carbonation, the CO$_2$ concentration in the atmosphere is 0.04% (Jerga, 2004, Sohail et al., 2018). This concentration can be increased from 0.4% to 20% if an accelerated carbonation test is carried out in the laboratory (Jerga, 2004, Xiao et al., 2002, BSI, 2013, Galan et al., 2013). In contrast, the carbonation curing requires pure CO$_2$, with a pressure of 1 bar or higher (Li et al., 2018b, Monkman and Shao, 2006). The higher CO$_2$ concentrations and pressure for carbonation curing enable a faster carbonation reaction.
2.5 Factors influencing carbonation curing

The potential effects of the carbonation curing on the properties and reaction products of cementitious matrices have been discussed in detail in Section 2.4. It has been stated that it is beneficial to have a higher degree of carbonation because carbonation curing can not only enhance the early strength of cementitious materials, but also sequester CO₂. Therefore, it is of interest to know the factors affecting the degree of carbonation.

The CO₂ reactivity and CO₂ diffusivity are two reasons that may affect the degree of carbonation (Fernandez Bertos et al., 2004). Reactivity mainly refers to the ability of the reaction of CO₂ with the samples, and diffusivity refers to the availability of CO₂ entering the samples. The key factors that might affect the reactivity and diffusivity of CO₂ are shown in Figure 2.3.

![Diagram showing factors influencing the degree of carbonation](image)

**Figure 2.3 Factors influencing the degree of carbonation (Fernandez Bertos et al., 2004)**

To evaluate the effects of carbonation curing, both the compressive strength and CO₂ uptake after carbonation curing are considered.
2.5.1 Compositions of raw materials

It is the solid compositions of the raw materials that determine the degree of carbonation. The effects of different cementitious materials on the early strength and CO₂ uptake are summarized in Table 2.4. To eliminate the effects of preconditioning, only samples without preconditioning are listed for comparison.

The strength of calcium silicates increases noticeably after carbonation. After 81 minutes' carbonation curing, the compressive strength of a C₃S and β-C₂S mortar developed from barely measurable to 70 MPa and 52.7 MPa, respectively (Young et al., 1974). The strength increase was attributed to the consumption of calcium silicates that increases the amount of C-S-H gel and CaCO₃ (Shtepenko et al., 2006, Young et al., 1974). It is worth noting that γ-C₂S, which is considered inert in the cement industry, is reactive under carbonation curing (Guan et al., 2016, Mu et al., 2018). The strength of the γ-C₂S paste increased from barely measurable to 52.92 MPa in 2h (Mu et al., 2018).

Mineral additions, such as GGBS and fly ash, can also be carbonated (Monkman and Shao, 2006). Free CaO or CH are the two common phases to be carbonated. Although it was found that the GGBS and fly ash contain 38.5% and 29.6% CaO from the XRF data, free CaO or CH cannot be detected from the GGBS. The carbonation of the GGBS cannot be attributed to any specific phase. In contrast, free CH is a main crystalline phase in the fly ash, which can be carbonated.
Table 2.4 Effects of carbonation on early compressive strength of different materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Sample size (mm)</th>
<th>w/c ratio</th>
<th>Carbonation duration (min)</th>
<th>Compressive strength (MPa)</th>
<th>CO₂ uptake (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S mortar (s/c = 1:1)</td>
<td>ø15.9×19</td>
<td>0.125</td>
<td>81</td>
<td>8</td>
<td>70</td>
<td>(Young et al., 1974)</td>
</tr>
<tr>
<td>β-C₂S mortar (s/c=1:1)</td>
<td>ø15.9×19</td>
<td>0.125</td>
<td>81</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-C₂S paste*</td>
<td>ø20×20</td>
<td>0.15</td>
<td>2h</td>
<td>13.16</td>
<td>52.92</td>
<td>(Mu et al., 2018)</td>
</tr>
<tr>
<td>C₃A</td>
<td>ø31×30</td>
<td>0.08</td>
<td>5</td>
<td>1</td>
<td></td>
<td>(Berger and Klemm, 1972)</td>
</tr>
<tr>
<td>Cement ø</td>
<td>76×127, depth is no less than 13</td>
<td>56.8</td>
<td>12.5</td>
<td></td>
<td></td>
<td>(Monkman and Shao, 2006)</td>
</tr>
<tr>
<td>Lime</td>
<td>with</td>
<td>24.0</td>
<td>23.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GGBS</td>
<td>0.15</td>
<td>8.7</td>
<td>6.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly ash</td>
<td>2h</td>
<td>3.5</td>
<td>11.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Note: all samples were moulded with a compaction force of 8 MPa; for *, the paste sample was moulded with a compaction force of 30 MPa. The samples were then put in a chamber containing purified CO₂ under a pressure of 4 bar or 5 bar. Since carbonation curing started immediately after casting, the strength of the reference samples was 0 or very low; for ø, cement was Canadian Standards Association (CSA) Type 10 cement)
2.5.2 Degree of hydration

The degree of hydration affects carbonation in two ways, namely, through the carbonation reactivity and the transport of CO\textsubscript{2} (Fernandez Bertos et al., 2004). With different degrees of hydration, the components in the samples prior to carbonation are different, which may affect the CO\textsubscript{2} reactivity. In addition, the CO\textsubscript{2} diffusivity can also be affected as a higher degree of hydration contributes to a lower permeability (Neville, 2011).

The effects of degree of hydration on carbonation reactivity are mainly due to the difference in the carbonation reactivity between the calcium silicates, and their hydration products, CH and C-S-H gel. The heat generated from the carbonation of C\textsubscript{3}S is higher than the carbonation of CH, which indicates a higher carbonation reactivity of C\textsubscript{3}S (Goodbrake et al., 1979); however, the rate of carbonation of CH is not a restricting factor as the carbonation of CH is a rapid precipitation reaction (Visser, 2014). The rate of the carbonation of C-S-H gel was lower than that for the carbonation of CH, as observed in the previous study (Berger et al., 1972). Studies by Trapote-Barreira et al. (2015) and Haga et al. (2005) also showed the higher dissolution rate of Ca\textsuperscript{2+} from CH than C-S-H gel, so the carbonation of C-S-H may be the restricting factor in the carbonation curing process.

As seen in Eqs. 2.13 and 2.14, with a low degree of hydration, the rates of the carbonation of C\textsubscript{3}S and C\textsubscript{2}S are high and the reactions rapidly produce CaCO\textsubscript{3} and C-S-H gel when exposed to CO\textsubscript{2} (Berger et al., 1972). Then the rate of carbonation of C-S-H gel is slower and becomes the restricting factor (Berger et al., 1972). With a high degree of hydration, the CH and C-S-H gel content are high, and CH is carbonated first. Then the CaCO\textsubscript{3} and C-S-H gel are present (Groves et al., 1991, Thiery et al., 2007), and the carbonation of C-S-H gel also becomes the restricting factor. In summary, different degrees of carbonation make no difference in the rate of carbonation, and the carbonation of C-S-H gel is the restricting factor.
Diffusivity is another important factor that is influenced by the degree of hydration. This is different for samples with originally low or high w/c ratios. For the concrete with a low original w/c ratio (~ 0.15), preconditioning is not required and carbonation is usually started immediately after casting. At this time, the compositions in concrete are almost the same as those of the raw materials. It mainly consists of alite, belite and calcium aluminates. For the samples with low w/c ratio, the moulding is normally formed by compaction, with appropriate compaction forces being applied (Fernandez Bertos et al., 2004, Farahi et al., 2013). However, if the compaction force is too high, it could lead to a lower carbonated strength because the diffusivity the CO$_2$ is too low for effective carbonation curing (Fernandez Bertos et al., 2004). In other words, the diffusivity of the concretes with lower w/c ratio is largely determined by the compaction force.

For concrete with a higher w/c ratio (0.3 ~ 0.6) than that required for carbonation (0.15), preconditioning must be performed before carbonation and this normally takes 4 hours to 18 hours, so that a noticeable degree of hydration has already occurred (Shi et al., 2012a, Morshed and Shao, 2014, El-Hassan and Shao, 2014b). Then the degree of hydration affects diffusivity in two ways, the remaining water content and permeability.

After the samples are mixed and vibrated, the water content is the primary reason that restricts the transport of CO$_2$, and the presence of liquid water can reduce the rate of CO$_2$ transport by several orders of magnitude (Sormeh Kashef-Haghighi, 2010). However, the pore water inside the specimens can be consumed through the hydration of the cement minerals. A study by Shi et al. (2012a) showed that concrete in moist conditions (higher than 98% RH) for a period of time (18h) has a higher degree of carbonation than the concrete carbonated immediately. This confirms that a higher degree of hydration would increase the rate of CO$_2$ transport. However, it is also known that the cement microstructure develops rapidly at early times (Neville, 2011). During normal hydration, a large volume of C-S-H gel is produced and contributes to a denser structure, which can lead to a lower permeability and lower rate of CO$_2$ transport (Neville, 2011).
In conclusion, the degree of hydration has little effect on the carbonation reactivity, but could influence the rate of the transport of CO₂ noticeably. This influence is achieved through changes to the remaining water content and the permeability of the concrete sample.

2.5.3 Water content

The water content is a critical parameter that influences the carbonation curing. A higher amount of water increases the dissolution of CO₂ and cement minerals, which is beneficial for the carbonation reaction. However, if the w/c ratio is excessive, the rate of transport of the CO₂ is slow which reduces the carbonation reaction as well. Therefore, there is an optimum w/c ratio for the carbonation reaction.

As the carbonation reaction increases compressive strength, the compressive strength can be used as the indicator for the degree of carbonation reaction. Berger and Klemn (1972) compacted the β-C₂S powder with w/c ratio of 0.10 ~ 0.175, and found that the optimum w/c ratio was 0.13, after which a rapid decrease in strength was noted. Klemn and Berger (1972) compacted the cement mortar with different w/c ratios, 0.06, 0.09, 0.19 and 0.28, respectively, and found that the w/c ratio of 0.09 achieved the highest strength after carbonation.

The optimum w/c ratio was between 0.13 and 0.18, and this is the main reason that some trials that cement, C₃S or C₂S powder with water, were conducted with w/c ratio of around 0.15 (Young et al., 1974, Monkman and Shao, 2006, Li et al., 2018b, Mu et al., 2018). Then the mixed powder and water were compacted before being put in the carbonation chamber.

However, this w/c ratio (below 0.18) is too low to be used for precast concrete to ensure the workability, both for the compacted and vibrated moulded concrete. To make this carbonation curing technology applicable for concrete with a higher w/c ratio, a preconditioning method is often used to remove a
certain amount of water before carbonation. Preconditioning methods are reviewed and discussed in more detail in Section 2.6.

2.5.4 Relative humidity

During normal carbonation, relative humidity (RH) is a determining factor for the degree of carbonation. An internal relative humidity of 50% ~ 60% is considered to be the optimum for normal carbonation, within which range there is sufficient water available for carbonation but not excessive in the capillary pores to impede the transport of CO$_2$ (Neville, 2011). Due to this reason, a specific relative humidity (RH) was set for most of the carbonation experiments.

In the study by Galan et al. (2013), after the cement paste specimens (size of 10 × 10 × 10 mm were prepared, the samples were preconditioned at specific relatively humidity (11%, 23%, 33%, 53%, 63%) for 50 days before exposing to 1 bar CO$_2$ pressure for 8-12 h. It was found that the 53% RH was the optimum humidity, which resulted in the highest rate of carbonation. However, for the C$_3$S and C$_2$S powders without being cast, the optimum humidity was 80% and 100% respectively, higher than that for normal carbonation (Goodbrake et al., 1979). This could be explained considering that the carbonation curing of the powder sample does not include the CO$_2$ transport from the atmosphere into the samples. As a result, the CO$_2$ transport of powder samples is not as important as that of cube or cylinder samples. For the powder sample, it is more important to have sufficient dissolved CO$_2$ in water, and thus a higher RH for carbonation curing of powder samples was expected.

For the cube or cylinder samples, a large amount of heat was generated by the carbonation curing for the cementitious specimens and water is immediately evaporated when the sample is exposed to CO$_2$, thus increasing the RH to 100% inside the carbonation chamber (Monkman and Shao, 2006, Zhan et al., 2013). This high RH may cause an impediment of CO$_2$ transport in the capillary pores.

Economics must also be considered in the context of the humidity control during carbonation curing because this represents an engineering problem. Current
efforts to control the humidity of the fresh concrete samples are not efficient, and it appears that even when the total water content is reduced to 40%, there is still an internal relative humidity above 95% at the surface of the sample (Morshed and Shao, 2014). Silica gel is used during carbonation curing to avoid water accumulation, but it has been found that silica gel is unable to absorb sufficient water vapour (Zhan et al., 2013), with the humidity rising to 100% immediately after carbonation and remaining at above 95% during the carbonation process.

In summary, carbonation curing releases water which raises the RH to 100%, and thus reduces the degree of carbonation for the carbonation curing process. However, in the engineering practice, it is inefficient to control the RH to the optimum level.

### 2.5.5 Carbonation time

A longer carbonation time generally contributes to a higher degree of carbonation and related higher compressive strength (Wang et al., 2017a, Pan et al., 2017, Ahmad et al., 2017). This can be explained by that the CO$_2$ diffuses gradually into the samples with time, which can be described by Fick’s second law (Eq. 2.13) (Basheer et al., 2001).

$$\frac{\partial \varphi}{\partial t} = D \frac{\partial^2 \varphi}{\partial x^2}$$  \hspace{1cm} (2.13)

where $\varphi$ is the concentration at location $x$, $t$ is time, $D$ is the transport coefficient, and $x$ is the location.

Therefore, the degree of carbonation increases rapidly at first and the rate slows gradually. Figure 2.4 shows the strength development of a C$_3$S paste as a function of carbonation time. After 27 minutes, the strength increased much more slowly than in the previous growth period (Young et al., 1974).
Similar trends are also shown in other studies (Shi and Wu, 2008, Wang et al., 2017a). After a critical carbonation time, the increase rate of the compressive strength and CO$_2$ uptake reduce. This can be explained by the less permeable outer layer of samples due to the expansive carbonation reaction, which reduces the rate of transport of CO$_2$ after a critical carbonation time (Zhang and Panesar, 2018a, Zhang and Shao, 2018). As a consequence, in some cases, carbonation reaction cannot penetrate into the samples and only affect the surface of the sample (Ahmad et al., 2017, Zhang and Shao, 2016a, Mo et al., 2016). The inner layer is not affected by carbonation and can develop strength due to normal hydration.

It is worth noting that the rate of carbonation reaction is different for calcium silicates, CH and C-S-H gel, as been observed in the normal carbonation process (Groves et al., 1991, Thiery et al., 2007). CH tends to react much earlier than C-S-H gel due to the higher dissolution rate of Ca$^{2+}$ from CH than C-S-H gel (Trapote-Barreira et al., 2015, Haga et al., 2005). When the hydration of calcium silicates is sped up with carbonation curing, CH quickly carbonates,
but the C-S-H gel reacts at a much lower rate (Berger et al., 1972). The depletion of C-S-H gel is always accompanied by a total, or at least locally total, consumption of CH (Chen et al., 2006). Therefore, with a limited carbonation time, the CH and calcium silicates may have carbonated, but C-S-H gel is less affected. With a longer carbonation time, C-S-H gel can be carbonated and can even become the primary carbonation phase when CH has been consumed (Borges et al., 2010). In the carbonation curing reaction, the Ca$^{2+}$ ions are released from C-S-H that leave the remaining C-S-H gel with a lower Ca/Si ratio (Trapote-Barreira et al., 2015, Berger et al., 1972, Shtepenko et al., 2006, Morandeau et al., 2014).

In summary, carbonation time may affect both the rate of transport of CO$_2$ and the carbonation products.

### 2.5.6 CO$_2$ pressure

According to Section 2.2, the CO$_2$ pressure affects the rate of CO$_2$ transport from the outside to the inside of the sample and the CO$_2$ dissolution in water.

1. **The effect of CO$_2$ pressure on the rate of CO$_2$ transport**

The pressure can influence the rate of CO$_2$ diffusion due to the concentration gradient and pressure gradient.

Different CO$_2$ pressures also mean different CO$_2$ concentrations. This can be explained by the ideal gas law (Eq. 2.14). With a higher CO$_2$ pressure, there is a higher concentration of gas CO$_2$.

\[
P V = nRT \tag{2.14}\]

where P, V and T are pressure, volume and absolute temperature; n is the number of moles of gas; and R is the ideal gas constant.
The different concentrations are the driving force for the diffusion, as described in Fick’s first law.

\[ J = -D \frac{d\varphi}{dx} \]  

(2.15)

where J is the transfer of mass per unit area during a unit time interval; \( \varphi \) is the concentration; \( x \) is position. A higher CO\(_2\) pressure means a higher concentration gradient between the gas and the core the sample, thus increasing the CO\(_2\) diffusion.

The pressure gradient can also be the driving force for the penetration of CO\(_2\) (Phung et al., 2015, Zou et al., 2015). A higher pressure also means the transport of gas CO\(_2\) is much faster.

(2) The dissolution of CO\(_2\) in water can be described as Henry’s law (Carroll et al., 1991).

\[ C = \frac{K_p}{K_h} \]  

(2.16)

where \( K_p \) is the partial pressure of the gas, \( K_h \) is the Henry’s constant and C is the concentration of CO\(_2\) in pore water. From the equation, it is clear that a higher CO\(_2\) pressure gives rise to a higher concentration of CO\(_2\) in pore water.

\( K_h \) is related to temperature and can be estimated based on Eq. 2.17.

\[ K_h = K_h^0 \ e^{-C \cdot \left( \frac{1}{T_0} - \frac{1}{T} \right)} \]  

(2.17)

where \( K_h^0 \) is the Henry’s constant at 298K, \( T_0 \) is 298K, and C is the temperature dependent constant.
From Eq. 2.18, it can be seen that a higher temperature would lead to a lower Henry’s constant, thus the concentration of CO$_2$ in solution would be lower with a specified pressure (Carroll et al., 1991).

The concentration of CO$_2$ in pore solution can also be the driving force for the transport of CO$_2$. As a consequence, a higher partial pressure of CO$_2$ can also increase the rate of transport of dissolved CO$_2$ in the pore water.

Therefore, the pressure can influence the degree of carbonation by influencing the rate of transport of CO$_2$; the pressure can possibly influence the carbonation products due to its effect on the rate of dissolution of CO$_2$. From the viewpoint of the thermodynamic process, different concentrations of CO$_2$ may result in the similar carbonation products (Visser, 2014). However, from the viewpoint of the dynamic process, a higher pressure may result in different carbonation products (Marta Castellote, 2009, Groves et al., 1991). Nonetheless, there is limited study regarding the effect of CO$_2$ pressure on the carbonation products.

The influence of the CO$_2$ pressure on concrete with and without preconditioning is summarized in Table 2.5.

<table>
<thead>
<tr>
<th>Carbonation time</th>
<th>Pressure (bar)</th>
<th>Strength (%)</th>
<th>Uptake</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$S mortar</td>
<td>1</td>
<td>100</td>
<td>N/A</td>
<td>(Young et al., 1974)</td>
</tr>
<tr>
<td>(without</td>
<td>2</td>
<td>192</td>
<td></td>
<td></td>
</tr>
<tr>
<td>preconditioning)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concrete</td>
<td>2h</td>
<td>0.7</td>
<td>100</td>
<td>10.5%</td>
</tr>
<tr>
<td>(with</td>
<td>1.4</td>
<td>107</td>
<td>13.1%</td>
<td></td>
</tr>
<tr>
<td>preconditioning)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>118</td>
<td>17.5%</td>
<td></td>
</tr>
</tbody>
</table>

(Note: For C$_3$S mortar (without preconditioning), the experiment was sealed with fixed amount of CO$_2$ added. By contrast, in the concrete (with preconditioning), CO$_2$ is supplied continuously after the consumption.)
Table 2.5 shows that a higher pressure can increase both the strength and CO$_2$ uptake of concrete. The increase is noticeable at lower pressures but is less apparent at higher pressures. As discussed before, a higher CO$_2$ pressure can increase both the transport of CO$_2$ and the dissolution of CO$_2$ in water. The increased transport can be evidenced by the fact that the degree of carbonation increased (Ahmad et al., 2017, Shi and Wu, 2008). However, the increase in the rate of transport is not linear with the increase of pressure because the initial carbonation reduces the permeability on the surface of the sample and retards later carbonation (Zhang and Panesar, 2018a, Zhang and Shao, 2018). When the permeability on the surface of the sample is low enough, the increase in the pressure may be difficult to further increase the rate of transport of CO$_2$ (Zhang and Panesar, 2018a, Zhang and Shao, 2018). Though generally an increase in the CO$_2$ pressure increases the carbonation efficiency and strength development, the rate of increase is much lower after the optimum pressure. Considering that a higher pressure also means a higher cost, selection of a suitable CO$_2$ pressure by balancing the carbonation efficiency and the cost is, therefore, needed. This can be the main reason that an optimum pressure, 2 bar (Young et al., 1974), 0.7 bar (Shi and Wu, 2008) and 2.1 bar (Ahmad et al., 2017), was found in the previous studies.

In addition, a higher peak temperature was found in the samples with higher pressure, indicating the carbonation reaction is more violent at higher pressures (Shi and Wu, 2008), which may be possibly due to the higher dissolution of CO$_2$ in pore water. The higher dissolution of CO$_2$ may affect the rate of carbonation reaction.

In summary, a higher CO$_2$ pressure increases the rate of transport of CO$_2$ and the dissolution of CO$_2$. An optimum CO$_2$ pressure exists which may be due to the reduced permeability of the carbonated samples.
2.6 Preconditioning methods

As discussed in Section 2.5.3, the water content is a critical factor that influences the rate of CO$_2$ transport during the carbonation curing process. The cement paste with low w/c ratio (0.15) can be compacted and then subjected to immediate carbonation curing successfully (Monkman and Shao, 2006, Young et al., 1974). The concrete can also be cast by compaction or vibration before carbonation curing, but as the concrete contains a higher water content than the optimum w/c ratio (0.15), preconditioning is needed before the carbonation curing (Zhang et al., 2016, Zhang and Shao, 2016a, Zhang and Shao, 2016b, Shi and Wu, 2008, Rostami et al., 2011). In this section, different preconditioning methods are reviewed to give some insights into how preconditioning methods are performed and how they affect carbonation curing, as seen in Table 2.6.

The most popular preconditioning method is to place the samples in an environment at a lower humidity for a period of time. The water requirement for concrete specimens cast by compaction is lower than that required for carbonation curing. Shi et al. (2012a) cast the lightweight concrete by compaction and then the concrete specimens were preconditioned in the environment with RH 55±10% and 20°C for 4h. The preconditioning process evaporated 4.5% of the water added. Compared with the steam cured counterparts, the 2h carbonation cured concretes reached 80% compressive strength of the steam cured specimens. He et al. (2016) cast concrete specimens by compaction, and then preconditioned them with RH 60% and 22°C for 4h. It was found that the preconditioning process evaporated 32% of the water added, and the carbonated strength of the concrete increased by 43% than that of the samples before carbonation.

Then CO$_2$ transport becomes a more complex issue when the concrete is cast by vibration. Trials have first been made to samples with vibrated compaction of zero-slump concrete. EI-Hassan et al. (2014b) cast the lightweight concrete with compaction using a vibrating hammer. Then the samples underwent air curing (24°C and RH of 50%) for 2h before being put in the carbonation chamber for
During the carbonation period, the RH inside the carbonation chamber was maintained at 50%, which can be considered as a water evaporation process as well. The water loss during the carbonation chamber was not calculated. Compared with the steam cured samples, the carbonation cured samples reached 90% of their strength. Morshed and Shao (2014) cast the concrete with compaction and vibration and then subjected to fan drying at 40-55% RH and 30°C for 4h. The water loss was around 52% after preconditioning, and the compressive strength achieved after carbonation curing was 450% of the air cured samples.

Comparing the concrete specimens subjected to vibrated compaction with concrete specimens subjected to compaction only, it can be found that it was generally more difficult to precondition the concrete specimens cast by vibrated compaction. This can be inferred from the stricter preconditioning condition used (fan drying) (El-Hassan and Shao, 2014b). This is because concrete subjected to vibration often leads to a surface saturation which impedes CO₂ transport.

There are also studies regarding the application of carbonation curing to concrete cast by vibration only. Rotami et al. (2012a) cast cement paste samples by vibration and then the paste specimens were preconditioned in the environmental chamber for 18h at a RH of 60% and 25°C for 20h. The preconditioning process lost 40% of the mixing water. Compared with air curing without carbonation, the compressive strength after carbonation increased by 61% with the CO₂ uptake of 8.9%. Zhang and Shao (2016) cast the concrete specimens by vibration, and then the specimens were preconditioned for 5h in-mould to reach initial set (25°C and RH 60%) and then demoulded and subjected to ambient condition (25°C and RH 50%) at a wind speed of 1m/s for 6.5h. Around 40% of water was lost from the samples during preconditioning and the compressive strength obtained after preconditioning and carbonation for 12h was 121% of the air cured samples.
Some trials of removing water have been applied to the carbonation curing process, so that the carbonation curing process also includes the preconditioning. Pan et al. (2017) cast mortar samples by vibration and then the samples were covered with plastic sheet for 24h at 20°C. Then the mortar specimens were carbonation cured with the RH of 70% maintained. Compared with the air preconditioned samples before carbonation, a 18% higher compressive strength was obtained. Ahmad et al. (2017) also cast the concrete samples by vibration and covered the sample with plastic sheet. There was no humidity control over the carbonation period. The carbonation curing duration for 2h exhibited no significant influence on the compressive strength.

There is an exception where a different preconditioning method was used - steam curing, (Rostami et al., 2011). The zero-slump concrete specimens were formed by vibration and exposed to steam curing (63°C) for 2h then followed by carbonation curing. The high temperature of the steam cured samples removes water before carbonation curing. As the concrete specimens were placed in the carbonation chamber immediately after steam curing, it is not precisely accurate how much water is lost due to the high temperature. Compared with the air cured samples after steam curing, there was no obvious strength development, with 9% CO₂ uptake.

From the discussions above, it can be found that the preconditioning for the concrete cast by vibration only takes a long time. One reason is that the water saturation is more severe when cast by vibration only. The other reason is that in order to satisfy the requirements for vibration, concrete generally has a higher water content to satisfy the workability. As a consequence, more water is needed to be removed for the subsequent carbonation curing. In this case, it is unavoidable that preconditioning time is prolonged.

However, as discussed in Section 2.4.4, the rapid strength development is a unique advantage of the carbonation curing technique. The carbonation process normally takes 2h to achieve a considerably high strength. However, the preconditioning time is long for the precast concrete, and particularly for
those cast by vibration only (11.5 ~ 24h) – the most widely used casting technique. The entire preconditioning and carbonation curing process, therefore, is long. Apparently it would be more beneficial if the preconditioning time can be reduced, as the strength development is most rapid in the carbonation curing process. Therefore, a more efficient preconditioning method is required for the subsequent carbonation curing.
Table 2.6 Effects of preconditioning methods on the carbonation curing of concrete

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Size (mm)</th>
<th>Way of moulding</th>
<th>Preconditioning methods to reach the water loss</th>
<th>Water loss (%)</th>
<th>Relative compressive strength (%)</th>
<th>CO2 uptake (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>cement, lightweight aggregate, sand</td>
<td>Ø100×100</td>
<td>Compaction</td>
<td>RH 55% humidity (4h)</td>
<td>4.5</td>
<td>80 (compared to steam curing)</td>
<td>17.5</td>
<td>(Shi and Wu, 2008, Shi et al., 2012a)</td>
</tr>
<tr>
<td>Cement, gravel, sand</td>
<td>Ø50×100</td>
<td>Compaction</td>
<td>RH 60% (4h)</td>
<td>32</td>
<td>143</td>
<td>N/A</td>
<td>(He et al., 2016)</td>
</tr>
<tr>
<td>Cement, lightweight expanded slag aggregate</td>
<td>127×76×38</td>
<td>Compact formed using vibrating hammer</td>
<td>RH 50% (N/A)</td>
<td>N/A</td>
<td>90 (compared to steam cured samples)</td>
<td>12.9</td>
<td>(El-Hassan and Shao, 2014b)</td>
</tr>
<tr>
<td>Cement, granite aggregate</td>
<td>127×76×40</td>
<td>Vibration compaction</td>
<td>RH 50% at 30 under forced fan drying</td>
<td>52</td>
<td>450</td>
<td>7</td>
<td>(Morshed and Shao, 2014)</td>
</tr>
<tr>
<td>Cement, crushed granite</td>
<td>127×76×40</td>
<td>Vibration</td>
<td>Steam curing (2 h)</td>
<td>12.3</td>
<td>89 (compared to steam cured samples)</td>
<td>9</td>
<td>(Rostami et al., 2011)</td>
</tr>
<tr>
<td>Raw materials</td>
<td>Size (mm)</td>
<td>Way of moulding</td>
<td>Preconditioning methods to reach the water loss</td>
<td>Water loss (%)</td>
<td>Relative compressive strength (%)</td>
<td>CO2 uptake (%)</td>
<td>Reference</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------</td>
<td>-----------------</td>
<td>-----------------------------------------------</td>
<td>----------------</td>
<td>----------------------------------</td>
<td>----------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Cement</td>
<td>14×14×6</td>
<td>Vibration</td>
<td>RH 60% at 20°C (18 h)</td>
<td>40</td>
<td>161 (compared to air cured samples)</td>
<td>8.9</td>
<td>(Rostami et al., 2012a)</td>
</tr>
<tr>
<td>Cement, sand</td>
<td>40×40×40</td>
<td>vibration</td>
<td>hydration in sealed mould</td>
<td>N/A</td>
<td>118% (compared to air cured samples)</td>
<td>N/A</td>
<td>(Pan et al., 2017)</td>
</tr>
<tr>
<td>Cement, fly ah, granite aggregate, superplasticizer</td>
<td>50×50×50</td>
<td>vibration</td>
<td>hydration in sealed mould</td>
<td>N/A</td>
<td>190% (compared to air cured samples)</td>
<td>N/A</td>
<td>(Ahmad et al., 2017)</td>
</tr>
<tr>
<td>Cement, coarse and fine aggregate</td>
<td>100×100×100 (concrete)</td>
<td>Vibration</td>
<td>In-mould curing for 5 hours (RH 60%), then off-mould preconditioned with wind at a speed 1 m/s (RH 50%) for 5-6 hours</td>
<td>40</td>
<td>119 (compared to air cured samples)</td>
<td>N/A</td>
<td>(Zhang and Shao, 2018, Zhang and Shao, 2016a)</td>
</tr>
</tbody>
</table>
2.7 Concluding remarks

In this chapter, the process, mechanism, effects of carbonation curing for cementitious materials and its influencing factors have been reviewed, and the following conclusions can be made.

- The controlling step for carbonation curing of cement is the rate of transport of CO\(_2\), and any factor affecting the rate of CO\(_2\) transport can influence the degree of carbonation.
- Carbonation curing provides a rapid strength gain and a certain degree of CO\(_2\) uptake, which implies a promising curing method for concrete.
- Mineral additions, such as fly ash, GGBS and limestone, can decrease the carbonation reactivity in the sample but also increase the rate of CO\(_2\) transport in the samples.
- A higher degree of hydration increases the rate of transport of CO\(_2\) by consuming the capillary water, but it also decreases the permeability of the concrete, which the rate of transport of CO\(_2\).
- Higher partial pressure of CO\(_2\) contributes to a higher carbonation degree, but the growth rate slows after reaching a critical point. The CO\(_2\) pressure may affect the carbonation products and carbonation depth.
- The longer the carbonation time, the higher the carbonation degree can be achieved. However, after reaching a critical point, the rate of increase in carbonation degree decreases. The carbonation time may influence the carbonation products and carbonation depth.
- Carbonation curing requires a low w/c ratio (around 0.15), which can only be used in compaction of paste or mortar. When carbonation curing is applied to vibrated concrete or concrete with compaction, preconditioning has to be used to remove water prior to the carbonation.
- Current preconditioning methods take a long time (11.5 ~ 18h) for the vibrated concrete, which is much longer than that for the carbonation curing (normally within 2h).
• An efficient preconditioning method is required to shorten the time required for preconditioning and to widen the application of carbonation curing in regard to concrete.

To sum up, carbonation curing can enhance early strength and absorb CO₂, but the normally vibrated concrete cannot be subjected to carbonation curing directly because its water content is too high which greatly reduces the subsequent carbonation efficiency. Preconditioning process is proposed to remove water prior to carbonation curing. In addition, the current preconditioning methods are inefficient and take a long time. Therefore, an efficient preconditioning method is required.
Chapter 3  Potential of using microwave heating as a preconditioning method for accelerated carbonation curing

3.1 Introduction

In this chapter, the mechanism of microwave heating and the dielectric properties of the components of concrete are reviewed. Following this, the effects of microwave heating on cementitious materials in terms of curing and drying are discussed. Finally, the potential of microwave heating as an alternative preconditioning method for accelerated carbonation curing is identified and proposed.

3.2 Mechanism of microwave heating

3.2.1 Introduction

Microwaves are a form of an electromagnetic wave which consists of an electric component and a magnetic component. In most applications, no matter whether it be in the food industry or in the concrete industry, the magnetic interactions are small, so only the electric component of microwave is usually considered (Hong and Oral, 1998).

Microwave energy can be directly converted into the heat through absorption by dipolar molecules in materials, so it is widely used for heating, such as in the microwave oven for everyday life. In addition, its unique heating mechanism also forms the basis of an efficient drying method, which has already been widely used in food and timber industry (Al-Duri and McIntyre, 1992, Nijhuis et al., 1998, Zielonka and Dolowy, 1998, Soysal, 2004, Zhang et al., 2006, Bal et al., 2010). The mechanism of microwave heating is reviewed in detail in the following section.
3.2.2 Microwave energy conversion

The electric energy of the microwave influences the asymmetric charge centre of dipolar molecules, such as water. The alternating electric field induces an alignment of the individual dipoles, but when the electric field decreases to zero, the dipoles return to their original positions, which is known as a relaxation process. The electric fields in microwaves oscillate rapidly, which change directions at a frequency of $2.45 \times 10^{9}$ times per second (~2.45 GHz in industry). The dipoles attempt to follow the changing electric field but always lag behind it, thus leading to vibration and friction and, as a result, converting the electromagnetic energy into thermal energy (Ong and Akbarnezhad, 2015, Mujumdar, 2006).

3.2.3 Dielectric properties

The ability of materials to interact with microwave energy is referred to as their dielectric properties. The dielectric property of a material can be described by Eq. 3.1 (Loupy, 2002)

$$
\varepsilon = \varepsilon' - j\varepsilon''
$$

(3.1)

where $\varepsilon$ is the complex dielectric constant; $j = \sqrt{-1}$; $\varepsilon'$ is the dielectric constant (the real part of the complex dielectric constant) which represents the ability of the material to store electric energy; and $\varepsilon''$ is the dielectric loss factor (the imaginary part of the complex dielectric constant) which represents the ability of the material to convert the electromagnetic energy into heat.

3.2.4 Penetration depth

With microwave heating, the electromagnetic energy can be converted into heat simultaneously, causing volumetric heating (Mishra and Sharma, 2016). The microwave energy penetrates into samples from the surface to the inside with energy lost gradually. When the energy has dropped to 37% ($1/e$) of that at its surface, the depth is defined as the penetration depth.
The parameters influencing the penetration depth are the wavelength, the dielectric constant, and the loss factor. The relevant equation is as follows (Metaxas and Meredith, 1993, Chandrasekaran et al., 2013).

\[
D = \frac{\lambda \sqrt{2}}{2\pi} \left[ \varepsilon' \sqrt{1 + \left( \frac{\varepsilon''}{\varepsilon'} \right)^2} - 1 \right]^{-1/2}
\]  

(3.2)

where \( D \) is the penetration depth and \( \lambda \) is the wavelength of the microwaves.

The Eq. 3.2 approximates to Eq. 3.3 for low loss dielectrics \( \left( \frac{\varepsilon''}{\varepsilon'} \ll 1 \right) \) is low (Metaxas and Meredith, 1993).

\[
D = \frac{\lambda \sqrt{\varepsilon'}}{2\pi \varepsilon'}
\]  

(3.3)

The power that can be absorbed by materials is dependent on the dielectric loss factor, as shown in Eq. 3.4. A higher dielectric loss factor leads to a higher amount of power absorbed.

\[
q = \pi f \varepsilon_0 \varepsilon'' |E|^2
\]  

(3.4)

where \( q \) is the energy absorbed by the sample, \( f \) is the frequency of the microwave, \( \varepsilon_0 \) is the permittivity of free space \( (8.85 \times 10^{-12} F \cdot m^{-1}) \), and \( E \) is the electric field intensity.
3.3 Effects of microwave thermal heating on cementitious materials

There has been considerable interest in the use of microwave energy as an alternative to conventional thermal energy of cementitious materials (Mangat et al., 2016, Makul, 2016, Kong et al., 2016). However, to achieve this goal, the cementitious materials need to have good dielectric properties. The dielectric properties of commonly used cementitious materials and their relevance to the penetration depth of microwave are, therefore, reviewed. In addition, the effects of microwave-based heating on the properties of cementitious materials are reviewed.

3.3.1 Dielectric properties and the penetration depth of cementitious materials

3.3.1.1 Introduction

It is the free water rather than the bound water which contributes more to the dielectric properties (Metaxas and Meredith, 1993). For concrete, free water refers to water held in the capillaries of the cement hydrates and absorbed in the aggregates, while bound water is mainly related to the chemically combined water in the cement hydrates (H.F.W.Taylor, 1997). At the beginning of hydration, free water quickly contacts with the cement particles and rapidly diminishes with time; then the concrete matures and the water is bound (Neville, 2011). As a consequence, the earlier the microwave energy is applied, the higher is the dielectric loss, which means a higher energy conversion efficiency. However, the penetration depth can also change accordingly with the changes in dielectric properties as shown below.

3.3.1.2 Dielectric properties and the penetration depth of the fresh cementitious materials

Figure 3.1 shows the evolution of dielectric properties (\( \varepsilon' \) and \( \varepsilon'' \)) and penetration depths of fresh mortar with initial w/c ratio of 0.45 (Makul, Keangin et al. 2010). The penetration depth is calculated based on Eq. 3.2. In this figure,
the dielectric constant and dielectric loss show a steady decrease with hydration time. The decrease was less significant at the beginning, but more noticeable after the initial setting time. This may be due to the conversion and evaporation of free water into the combined water and to the atmosphere. Due to the changes in the dielectric properties, the penetration depth increased constantly with the hydration time. The penetration depth was 16 mm at the immediate contact of cement with water, then increased to 20.4 mm just before initial setting and 36.7 mm at final setting. The penetration depth rose to 55.8 mm at 12h hydration. The trend is likely to continue with further hydration as the free water content is supposed to decrease steadily. In summary, the dielectric properties of the fresh concrete decrease while the penetration depth of the microwave energy increases with hydration time. This indicates that the microwave energy may not be able to penetrate through the fresh concrete at beginning but the penetration depth can increase rapidly when the concrete is heated by microwave energy.

Figure 3.1 The dielectric properties and penetration depth of fresh concrete (Makul, Keangin et al. 2010)
3.3.1.3 Dielectric properties and the penetration depth of matured mortar under different moisture conditions

Hong and Oral (1998) investigated the electromagnetic properties of a mortar at 28 days under different moisture conditions in comparison with those of water, cement and sand (shown in Table 3.1). Based on their results, the penetration depth was calculated with Eq. 3.2. The frequency of the wavelength was set at 2.45 GHz for the calculation.

Table 3.1 The dielectric properties of matured mortar under different moisture conditions (Hong and Oral 1998)

<table>
<thead>
<tr>
<th>Curing conditions</th>
<th>Dielectric constant</th>
<th>Dielectric loss</th>
<th>Penetration depth (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet</td>
<td>12</td>
<td>0.11</td>
<td>613.75</td>
</tr>
<tr>
<td>Saturated</td>
<td>6.7</td>
<td>0.08</td>
<td>630.58</td>
</tr>
<tr>
<td>Air dried</td>
<td>4.5</td>
<td>0.02</td>
<td>2067.13</td>
</tr>
<tr>
<td>Oven dried</td>
<td>4</td>
<td>0.01</td>
<td>3897.82</td>
</tr>
<tr>
<td>Water</td>
<td>77</td>
<td>13</td>
<td>13.16</td>
</tr>
<tr>
<td>Sand</td>
<td>2.2</td>
<td>0.018</td>
<td>1605.94</td>
</tr>
<tr>
<td>Cement</td>
<td>4</td>
<td>0.025</td>
<td>1559.13</td>
</tr>
</tbody>
</table>

From Table 3.1, it can be seen that a matured mortar has lower dielectric abilities at 28 days when compared with the fresh concrete shown above. This may be due to the lower free water content in the mature mortar. For the same reason, a wet mortar exhibits better dielectric properties than a saturated or dry mortar. This indicates that, in theory, a wet mortar can be quickly heated up by microwave and, hence, can effectively remove the moisture from mortar. The same could be true for paste and concrete.

Table 3.1 also shows that the microwave penetration depth for the matured mortar varies under different moisture conditions, which is much higher than that in the early stage. This further demonstrates that the dielectric properties reduce with ongoing hydration and, hence, the penetration depth is increasing as hydration proceeds. As a result, for concrete elements with different depths,
the microwave can penetrate through the concrete specimens at different stages.

As summarized above, the relatively good dielectric properties make microwave heating of cementitious materials possible, especially before setting. The penetration depth is relatively small at early age, but increases steadily with time.

### 3.3.2 Effects of microwave heating on the properties of cementitious materials

#### 3.3.2.1 Introduction

Microwave heating can be a potential technique for concrete manufacture. Compared with conventional thermal heating, it is considered that the microwave energy can be transferred to the materials much faster and more homogeneously, as discussed in Section 3.2.2.

When microwave heating was first introduced to the concrete industry, domestic microwave oven was used. With such microwave oven, the power output can only be set at a specific level, and thus the total power output can only be adjusted by the time. This is achieved by turning on and off the ‘start’ button. The biggest limitation for the domestic microwave oven is that it is unable to monitor the real-time temperature during the curing process, and the concrete can be easily overheated and be damaged. To overcome the limitations of domestic microwave oven, customised microwave system was designed to better control the quality of concrete. Some other modifications were also made to make the microwave heating suitable for industrial use.

Then this section reviews the detailed information on the pilot investigations of microwave heating, including domestic microwave oven and industrial microwave systems, on cementitious materials. The information is summarized in Table 3.2.
Table 3.2 The impact of microwave heating on strength of cementitious materials

<table>
<thead>
<tr>
<th>Microwave oven</th>
<th>Material</th>
<th>Size (mm)</th>
<th>w/c ratio</th>
<th>Delay time (min)</th>
<th>Power output/temperature (duration)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Domestic oven</td>
<td>PC mortar</td>
<td>40×40×40</td>
<td>0.44</td>
<td>0,45,120</td>
<td>150W (30 min)</td>
<td>(Wu et al., 1987)</td>
</tr>
<tr>
<td></td>
<td>PC mortar</td>
<td>40×40×160</td>
<td>0.44</td>
<td>0</td>
<td>Less than 50W (40 min)</td>
<td>(Hutchison et al., 1991)</td>
</tr>
<tr>
<td></td>
<td>PC mortar</td>
<td>15×40×200</td>
<td>0.5</td>
<td>0</td>
<td>40W (90 min), 80W (90 min)</td>
<td>(Pera et al., 1997)</td>
</tr>
<tr>
<td></td>
<td>Mortar and concrete with rapid hardening cement</td>
<td>φ76.2×152.4</td>
<td>0.5</td>
<td>30</td>
<td>300 ~ 600 W (45 min)</td>
<td>(Leung and Pheeraphan, 1995)</td>
</tr>
<tr>
<td></td>
<td>Mortar and concrete with rapid hardening cement</td>
<td>φ76.2×152.4</td>
<td>0.5</td>
<td>30</td>
<td>362W (30 min) + 275W (15min)</td>
<td>(Pheeraphan et al., 2002)</td>
</tr>
<tr>
<td></td>
<td>PC mortar</td>
<td>40×40×160</td>
<td>0.4, 0.5, 0.6</td>
<td>30, 45, 60,90</td>
<td>Power on and off with 90 W (30 ~ 60 min)</td>
<td>(Topçu et al., 2008)</td>
</tr>
<tr>
<td></td>
<td>PC paste</td>
<td>Φ69×40</td>
<td>0.38</td>
<td>30</td>
<td>390W (15 min) + 811W (15min) + 390W (15min)</td>
<td>(Natt Makul, 2011)</td>
</tr>
<tr>
<td></td>
<td>PC mortar</td>
<td>Φ40×80</td>
<td>0.45</td>
<td>30, 60, 120</td>
<td>Power on and off with (440W, 260W and 140 W)</td>
<td>(Kong et al., 2016)</td>
</tr>
<tr>
<td>Microwave oven</td>
<td>Material</td>
<td>Size (mm)</td>
<td>w/c ratio</td>
<td>Delay time (min)</td>
<td>Power output/temperature (duration)</td>
<td>Reference</td>
</tr>
<tr>
<td>--------------------</td>
<td>--------------------------------------------------</td>
<td>----------------</td>
<td>-----------</td>
<td>------------------</td>
<td>--------------------------------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td></td>
<td>Concrete with rapid hardening cement</td>
<td>φ76.2×152.4</td>
<td>0.5</td>
<td>35</td>
<td>80°C (45min)</td>
<td>(Leung and Pheeraphan, 1997)</td>
</tr>
<tr>
<td>Industrial</td>
<td>PC paste</td>
<td>50×50×50</td>
<td>0.3, 0.35, 0.4, 0.45, 0.5</td>
<td>1440</td>
<td>11.2 kW (15 min or 30 min)</td>
<td>(Rattanadecho et al., 2008)</td>
</tr>
<tr>
<td>microwave system</td>
<td>PC Mortar</td>
<td>Φ50×100</td>
<td>0.4</td>
<td>30</td>
<td>60°C (62 min)</td>
<td>(Sohn and Johnson, 1999)</td>
</tr>
<tr>
<td></td>
<td>PC paste</td>
<td>Φ69×40</td>
<td>0.38</td>
<td>30</td>
<td>390W (15 min) + 811W (15 min) + 390W (15 min)</td>
<td>(Natt Makul, 2011)</td>
</tr>
<tr>
<td></td>
<td>Concrete</td>
<td>150×150×150</td>
<td>0.5</td>
<td>15, 30, 45 min</td>
<td>800W (15 ~ 45 min)</td>
<td>(Makul et al., 2017)</td>
</tr>
</tbody>
</table>
3.3.2.2 Domestic microwave oven

In the steam curing process (conventional thermal curing), the concrete is normally exposed to ambient temperature for around 3 to 5 hours before the temperature rise, which is also known as the delay time (Yazıcı et al., 2005, Gonzalez-Corominas et al., 2016). This delay is to allow the cementitious materials to develop sufficient strength to withstand the tensile stresses, which could be generated due to the temperature gradient, that develops inside the concrete. However, the delay time before heating is much shorter with microwave heating than that of steam curing.

Wu et al. (1987) studied the properties of PC mortar samples, and found that the optimum curing regime was to set a constant output power of 150W for 30 min, and the 28d strength was improved after the microwave-based heating regime. In addition, the study compared the effect of delay time of 0, 45, and 120 min on the compressive strength after 3 days. It was found that the delay time of 0 min was the optimum. Hutchison et al. (1991) heated the PC mortar with microwave energy immediately after casting, and also found that the microwave energy accelerated the curing of PC mortars without reducing the long term strength. Pera et al. (1997) also cured the PC mortar without any delay time.

In the study by Leuang and Pheeraphan (1995), the concrete and mortar samples were prepared with Type III cement (rapid hardening cement). The effect of the delay time of 20, 30, 40 and 61 min on the compressive strengths at different ages was compared, and 30 min was found to be the optimum. In the later study by Pheeraphan et al. (2002), the delay time of 30 min was directly applied to the concrete samples prepared with Type III cement. Topcu et al. (2008) investigated the effect of delay time of 30, 45 and 60 min on the 6h and 7d strength, and found that the optimum delay time was 30 min. In the study, the microwave power was turned on a period of time, and then off for some time. The total microwave heating time ranged from 30 to 60 min. Makual and Agrawal (2011) applied a delay time of 30 min to the PC paste without any further explanation. Kong et al. (2016) controlled the temperature within the limit
by turning on and off the power for a period of time. The study compared a delay time of 30, 60 and 120 min in terms of their effects on the early strength, and found that the delay time was insignificant. The study also found that the microwave heated samples achieved higher early and later strength compared with steam cured samples.

3.3.2.3 Industrial microwave systems

In order to apply the potential microwave heating technique to concrete industry, some efforts have been made to modify the domestic microwave oven, as shown in Table 3.2.

To address the issue that microwave power can easily overdry the cementitious specimens, a temperature feedback system was adopted by some studies (Leung and Pheeraphan, 1997, Sohn and Johnson, 1999, Shi, 2017). The system can adjust the microwave output power based on the temperature measured by a thermocouple or optical fiber inserted into the sample. Leung and Pheeraphan (1997) applied the delay time of 35 min. With the controlled temperature inside the concrete, the concrete specimens could achieve very high early strength without deterioration in later strength performance. In the study, the highest rate of temperature rise was 3.5°C/min and the curing time was 45 min. Sohn and Johnson (1999) also set the delay time of 30 min, and the rate of temperature rise achieved as high as 7°C/min. The study showed that for the PC mortar samples exhibited significant reduction in the 28d strength with the maximum temperature of 80°C. With controlled heating time, the mortar samples could achieve a higher 28d strength with the maximum temperatures of 40°C and 60°C.

Some other modifications for the microwave oven were made for industrial use. Rattanadecho et al. (2008) used a microwave continuous belt drier to conduct experiments on the cement paste, as shown in Figure 3.2. The microwave power was emitted by 14 magnetrons, with the total output power could be up to 11.2 kW. This enabled a continuous curing of the cementitious specimens at
an industrial level. The results showed that the microwave energy have the potential to cure cement paste to achieve high early strength and little reduction in long-term strength.

Makul and Agrawal (2011) applied an industrial microwave generator with a maximum power of 6.0 kW to the cementitious materials. The temperature was measured at the start and end of heating, and the delay time was set at 30 min.
The results showed that the cement paste developed strength rapidly after microwave heating.

Makul et al. (2017) employed a mobile microwave heating unit for concrete curing, which was constructed based on the mathematical models evaluated from the heat generation within a horn antenna. The study also investigated the delay time of 15 min, 30 min and 45 min, and 30 min was concluded to be the optimum. This study further demonstrates the effectiveness of microwave heating as an innovative curing method to accelerate the early strength of concrete.

3.3.2.4 Summary

In summary, the microwave heating as a curing method has a much shorter delay (0 ~ 90 min) time than steam curing (2 ~ 4h). In most studies, 30 min was demonstrated as the optimum preconditioning time. In addition, the increase rate of temperature for microwave heating is in the ranges of 3.5 ~ 7°C/min (Yazıcı et al., 2005, Gonzalez-Corominas et al., 2016), which is much higher than that for steam curing (10 ~ 45°C/h). The energy for microwave heating is transferred to concrete via volumetric heating (Ong and Akbarnezhad, 2015, Chandrasekaran et al., 2013), and the energy for steam curing is via conduction. As a consequence, the temperature gradient in the microwave heating is much smaller when compared with that in conventional heating during the temperature rise process, which leads to less tensile stress. For microwave heating, such a less tensile stress does not require the concrete to wait for such a long time, and the rate of temperature rise is also higher. Therefore, the microwave heating only needs a shorter delay time and can withstand a higher rate of temperature increase.
3.4 Effects of microwave non-thermal heating on the rate of reactions

Despite the effect of microwave heating described above, microwave irradiation has also been reported to have non-thermal effect on the chemical reaction due to its unique heating mechanism (Wang et al., 2006, Lin et al., 2009, Nomanbhay and Ong, 2017). The non-thermal effect refers to the phenomenon that the sintering process or chemical reaction induced by microwave heating is faster than that by conventional heating when they exactly have the same temperature history.

The non-thermal effect is still under debate. The opposition for the microwave non-thermal effect is the quantum energy of microwave is far too low to influence chemical reaction. The quantum energy calculated based microwave at 2.45 GHz is $1 \times 10^{-5}$ eV, far below Brownian motion with $2.7 \times 10^{-3}$ eV, hydrogen bond with $0.04 \sim 0.44$ eV and ionic bond with $7.6$ eV (Nomanbhay and Ong, 2017, Loupy, 2002). Thus, microwave energy could not break chemical bonds to create new reactions. The observed advantages of microwave energy might be due to the selective heating and inaccurate control of temperatures (Hoz et al., 2004, Shazman et al., 2007, Reddy et al., 2013).

However, there are also numeral studies claiming when they precisely controlled the temperature history, there is still an increased reaction rate for microwave heating (Wang et al., 2006, Lin et al., 2009, Nomanbhay and Ong, 2017). Though microwave energy is not high enough to break the chemical bonds, it is sufficiently high to lower the activation energy, as seen in Arrhenius’s equation (Eq. 3.5).

$$v = Ae^{-Ea/RT}$$  \hspace{1cm} (3.5)

where $v$ is the chemical reaction rate, $A$ is pre-exponential factors, $Ea$ is the activation energy, the energy required for the initiation of the reaction, $R$ is the universal gas constant, and $T$ is the absolute temperature.
If $E_a$, the activation energy, is reduced, the reaction rate is thus increased. There are numerical studies regarding the reduction of the activation effect of chemical reactions (Shibata et al., 1996, Wroe and Rowley, 1996, Janney et al., 2005). The reduction in activation energy can be attributed to the mechanism of microwave heating that rotates the dipoles, and thus increases the probability of the colliding of molecules and atoms. Shibata et al. (1996) compared the effect of conventional heating and microwave heating on the disintegration reaction of $\text{NaHCO}_3$, and it was found that the activation energy was reduced by the microwave radiation. Wroe and Rowley (1996) used a hybrid furnace to study the effects of microwave non-thermal effect on the sintering of partially stabilized zirconia, as shown in Figure 3.3. The shrinkage of the sample reflects the rate of sintering reaction. The hybrid furnace allowed the microwave and conventional heating to be varied during heating. The microwave heating was turned off when the temperature was around $1080^\circ\text{C}$, then the sintering stopped. Only after the temperature was elevated by around $100^\circ\text{C}$ with conventional heating, the sintering process continued. This clearly showed the microwave non-thermal effect increased the sintering reaction rate and was resulted from the reduced activation energy.
Figure 3.3 Normalized linear shrinkage of zirconia plotted as a function of sintering temperature for hybrid sintering showing the effect of switching off the microwaves during the process (\( \sim 1080^\circ C \)) (Wroe and Rowley, 1996)

Janney et al. (1991) studied the grain growth of the aluminum under conventional heating and microwave heating. The activation energy for microwave heating was around 20% lower than that for conventional heating, with 480 kJ/mol and 590 kJ/mol, respectively. The authors also attributed this to the difference in the transport rates for microwave and conventional heating. Wang et al. (2006) studied the sintering of three different ceramics by microwave heating and conventional heating using identical temperature histories. The microwave heating shows a better sintering performance than conventional heating, and the ceramics that has the best dielectric properties gave the most enhancement. This could be only attributed to the non-thermal effect by microwave heating. Li et al. (2009) investigated the removal of ammonia nitrogen from wastewater by microwave radiation and conventional heating, and also found the superior performance of microwave heating. This was mainly attributed to thermal effect and was enhanced by non-thermal effect. Fukushima et al. (2013) studied the reduction reaction of CuO with microwave heating and conventional heating. The microwave energy can be separated to electrical filed and magnetic field, and it was found that the activation energy reduced by 2/3 in the electrical field (117 kJ/mol) and by 1/3 in the magnetic field (228 kJ/mol) compared to that in conventional heating (292 kJ/mol).

The study of the non-thermal effect on cement hydration is limited. However, when applying microwave energy to cement hydration, the non-thermal effects could not be simply ignored due to the relatively good dielectric properties of clinker phases and the solvent, water. It should also be noted that compared with the thermal effect, the non-thermal effect is small.
3.5 Drying accompanied by microwave heating

Microwave heating of cementitious materials causes a temperature rise which is accompanied by water evaporation. In this section, the mechanism of drying is described first, then followed by the application of microwave heating in industrial drying. Finally, the water loss in the cementitious materials accompanying microwave heating is discussed.

3.5.1 Mechanism of drying

Generally, drying refers to the process of the removal of water from the solid materials. This occurs when the partial pressure of the vapour above the water is lower than the vapour pressure of water (saturated vapour pressure) at the same temperature. Heating and increased air flow are conventionally used drying methods. (a) Heating. When the temperature of water is elevated, its saturated vapour pressure increases, so the gap between the saturated vapour pressure of water and the partial pressure of the gas above the water is wider. As a consequence, drying is accelerated. (b) Airflow. With a lower partial pressure of vapour above the water than the saturated vapour pressure of water, the water molecules turn into vapour and enter into the air. Then the gap of the vapour pressure decreases locally until the vapour near the liquid water diffuses to elsewhere. As the airflow is speeded up, the vapour above the water can be locally reduced and then drying is accelerated.

Two simultaneous processes usually occur during drying, namely: (1) the removal or loss of water from the surface of the solid; and (2) the transfer of water from the inner part of the solid material towards the surface (Al-Duri and McIntyre, 1992). Figure 3.4 qualitatively shows a typical drying rate curve with three stages of water loss of a wet material. The three stages include first drying stage (constant rate stage), second drying stage (first falling rate stage) and third drying stage (second falling rate stage).
First drying stage: When the material is firstly exposed to heat, the water is lost at constant rate. In the stage, the surface of the material contains sufficient free water, and the factors determining the drying rate is external environment, such as relatively humidity, temperature, rate of airflow etc. With a higher temperature and higher rate of air flow, the constant rate increases (Chinenye, 2009, Velić et al., 2004). This stage continues until drying points of the surface start to appear on the surface of the solid materials.

Second drying stage: the rate of drying at this stage decreases as some areas becomes dry. However, the rate per unit wet solid surface of the solid material remains constant. The rate of drying is controlled by the surface of the wet area of the solid material and the external environment or transfer of moisture from the inner part to the surface. This is the transition stage from first stage to the third stage.

Third drying stage: when the whole wet surface becomes dry, the third stage occurs. The moisture gradient between the surface and the deeper parts is the
drying force for the transfer of the moisture. In this stage, the rate of the drying is controlled by the transport of moisture from the inside to the surface. And the transport of moisture is determined by the temperature, porosity etc. of the solid materials. A higher temperature and higher porosity generally increase the transport of the water (Karathanos et al., 1991, N. Marousis et al., 1991, Roca et al., 2006, Roca et al., 2008, Yang et al., 2017, Baik and Marcotte, 2003).

For samples with a high water content, drying starts from the first stage at a constant rate of drying. Sometimes only two stages are identified, the constant rate stage and second falling rate stage (third drying stage). In the former stage, the controlling factor is the rate of evaporation from the surface to the environment while in the latter stage, the controlling factor is the rate of movement of the water from the inner layers to the surface.

3.5.2 Mechanism of microwave drying

The unique mechanism for the microwave heating makes it different from the conventional drying. As for the conventional drying, the energy, normally heat, is transferred to the surface of the solid material, and the energy is then slowly transferred to the interior. In the meanwhile, the heat in the surface causes a dry surface, leaving the moisture to transfer from the interior to the surface slowly. The direction of the energy transfer and mass transfer is different. By comparison, the microwave heating produces homogeneous temperature throughout the solid materials, and the surface of the material is lower due to the evaporation. Thus the energy transfer and mass transfer have the same direction (Al-Duri and McIntyre, 1992). Due to the unique mechanism, microwave energy has been considered as an efficient drying technique (Soysal, 2004, Bal et al., 2010, Chandrasekaran et al., 2013, Zielonka and Dolowy, 1998, Maskan, 2001). This section reviews the application of microwave heating, mainly in timber and food industries.

Compared with conventional drying, microwave drying is more time-efficient. Soysal (2004) studied the microwave drying of parsley with different output powers. The drying comprises the constant rate period and falling rate period.
The study concluded that compared with hot air drying, microwave heating greatly reduce the drying time and produce good quality parsley products with green colour. Maskan (2001) compared the effects of microwave heating (210 W) and hot air drying (air velocity of 1.29 m/s, 60°C), and found that the microwave heating significantly decreased the drying time and only took 11% of air drying time.

With microwave heating, the rates of drying have been reported to be enhanced, particularly in the third drying stage. In the constant rate period (the first drying stage), water can evaporate because of the difference between the humidity of the surface of the sample and the environment, similar to that in conventional heating. Zielonka and Dolowy (1998) studied the drying rate of spruce with initial moisture content from 35% to 85%. The study showed that the constant rate period is extended by microwave heating, compared with the conventional drying method. This was attributed to the more effective transfer of energy to the water in the spruce.

Microwave heating is more beneficial during the third stage of drying, when transport of the moisture in the sample is a controlling factor (Zhang et al., 2006, Maskan, 2001, Guo et al., 2017, Maskan, 2000). In the third stage, the moisture content inside the samples is lower than the water content in the surface of the material (Brosnan, 2001). Then the moisture transfers from the interior to surface slowly due to the mass gradient. As discussed before, water is the main component which absorbs microwave energy. In this case, selective heating occurs and the area containing more moisture absorbs more microwave energy. A higher temperature could thus be achieved in the inner part than the surface. When the internal temperature is above 100°C, water inside the sample can turn into vapour, and this generates an internal pressure that moves water to the surface, the so-called ‘pumping effect’ (Song et al., 2016, Maskan, 2000, Bouraoui et al., 1993). This increased internal pressure is an extra force that moves a mass of liquid from the inside to the surface, and ultimately to the atmosphere. Therefore, the migration of moisture is significantly speeded up and the rate of drying is increased. Maskan (2000) used hot air (60°C and air
velocity of 1.45 m/s) to dry banana until the drying slows down. Then the drying was followed by microwave heating in the falling rate drying period. Compared with hot air drying, microwave heating reduces the drying time by 64.3%. This was attributed to the increased migration of moisture by microwave heating within the samples.

In summary, the microwave heating is an efficient drying method that extends the constant rate stage and is much more efficient in the falling rate stage by speeding up the transfer of moisture inside the solid materials.

3.5.3 Effects of microwave heating on drying cementitious materials

In the literature regarding the application of microwave heating to cementitious materials, the drying occurs simultaneously. The drying due to microwave heating is considered as an unique advantage, the so-called ‘densification effect’. When part of the free water is lost before the setting of cement, the capillary pores collapse and reduce. In this case, the long-term strength could be enhanced, which has been observed in some studies (Wu et al., 1987, Hutchison et al., 1991, Sohn and Johnson, 1999, Kong et al., 2016). The amount of water loss during microwave heating is reviewed below.

Wu et al. (1986) used microwave energy with fixed power output to heat the mortar samples with sample size of 40×40×40mm cubes at different power levels. The percent of water loss with respect to initial water content is presented in Figure 3.5. It was found that the water loss increases linearly with time and the loss could be as high as 51% (for microwave power 220 W) or 22% (for microwave power 150 W) when microwaving for 60 minutes.
Figure 3.5 Water loss from the mortar sample under fixed power (adapted from (Wu et al., 1987))

Leung and Pheeraphan (1997) investigated the water loss from concrete with sample size of $\phi 76.2 \times 152.4$ mm when the feedback control system was used at programmed temperatures, as seen in Figure 3.6. With microwave heating for a fixed time of 45 minutes, the percent of water loss was around 4.5%, much lower than the study by Wu et al. (1987). This may result from the fact that the sample size of the specimen was much larger. As water can only evaporate from the surface of samples, it is more difficult to remove water from the specimens with higher depths, as also shown in other works (Tahmasebi et al., 2011).
Makul et al. (2017) studied the water loss of concrete subjected to different microwaving time and power output. The percent of water loss relative to initial water was not given. However, it was obvious that significant amount of water was lost after microwave heating, and a longer microwave heating time evaporated a higher amount of water.

The process of the water evaporation under microwave heating is explained as follows. When microwave energy is applied, the concrete is in plastic stage. At first, drying starts with a high initial water content and the controlling factor for the rate of drying is the migration of moisture from the surface to the atmosphere. Then the drying rate decreases as the surface becomes dry, and the controlling factor becomes the transfer of moisture from the inside to the surface of the sample. However, the transfer of water is low and can be further lowered due to the stiffening or hardening of the cement. If the temperature
inside is high enough for turning water into vapour, the vapour would form extra pressure and create a ‘pumping effect’, thus increasing the migration of moisture (Song et al., 2016, Maskan, 2000, Bouraoui et al., 1993). In practice, the temperature must be controlled to below 70°C to avoid delayed ettringite formation in the concrete industry (Asamoto et al., 2017, Amine et al., 2017). In this case, the ‘pumping effect’ would not occur, but a similar phenomenon is expected though not shown in literature yet. It is known in vibrated concrete, around 2% air is entrapped in concrete during mixing (Liu and Hansen, 2015, Şahin et al., 2017). As the volume of the air voids can increase due to the expansion of the air bubbles under microwave heating (Pheeraphan and Leung, 1997), it is, thus, anticipated that these expanded voids inside the concrete could form a vapour path to the surface and these paths in turn increase the transport of the moisture inside the samples, resulting in a rapid rate of drying and a relatively more homogeneous water distribution.

In summary, the microwave heating on cementitious materials is accompanied by a significant amount of water loss, which may be beneficial to the strength due to the ‘densification effect’.
3.6 The potential of using microwave heating as a preconditioning method for carbonation curing

In the previous chapter, it was made clear that carbonation curing could lead to improved compressive strength and increased CO$_2$ uptake (Li et al., 2018b, Monkman and Shao, 2006). However, the application of carbonation curing is limited and cannot be applied to normally vibrated concrete, this is because the water content required for satisfying the workability of the normally vibration concrete (w/c ratio of 0.3 ~ 0.6) is higher than that for the optimum carbonation curing (w/c ratio of ~ 0.15) (Berger and Klemm, 1972, Monkman et al., 2009, Mu et al., 2018, Neville, 2011).

To solve this problem, different preconditioning methods have been used before carbonation curing to remove this ‘excess’ water. As discussed in Chapter 2, the most widely used preconditioning method is to make the concrete exposed to a lower humidity (Shi and Wu, 2008, Shi et al., 2012a, He et al., 2016) (Rostami et al., 2012a). To speed up the preconditioning efficiency, fan drying is also applied in some studies in addition to low RH (Zhang and Shao, 2018, Zhang and Shao, 2016a). However, their preconditioning efficiency is low. For the normally vibrated concrete, the preconditioning time (a low RH and fan drying) spent 11.5 ~ 20 hours to evaporate around 40% water of water added in to facilitate the subsequent carbonation curing (Rostami et al., 2012a, Zhang and Shao, 2016a). When the surface of the cementitious materials are subjected to an unsaturated vapour pressure (RH < 100%) and higher rate of airflow (fan drying), the water in the surface of the sample can be readily lost, but the rate of transfer of water from the inner part to the surface is low which is the controlling factor for the rate of drying. As the preconditioning takes a long time, the porosity may be lowered due to hydration and thus the rate of transfer of water is further reduced (Roca et al., 2008, Yang et al., 2017, Baik and Marcotte, 2003). With a low rate of transfer of water, it is assumed that the surface can be over-dry and the inner part loses less water. As a consequence, this preconditioning method is inefficient and the surface of the materials tends to be over-dry.
The other preconditioning method is steam curing prior to carbonation curing (Rostami et al., 2011). For this method, a very small amount of water is lost during steam curing as the vapour pressure on the surface of the material is saturated. The water is primarily lost after steam curing when the concrete was demoulded and subjected to low RH (30%). The high temperature of the material and low RH in the environment increased the rate of water loss from the surface to the environment. However, it is expected that the water loss due to the higher temperature cannot last long as the sample cools down rapidly.

Therefore, these preconditioning methods are inefficient; it either takes too much time, or requires a porous cementitious material. To make the whole process more efficient and to allow for a wider application of carbonation curing, the preconditioning method should be more efficient. In this study, microwave heating is proposed as an efficient preconditioning method.

As discussed before, microwave heating can be applied to cementitious materials due to their relatively good dielectric properties (Makul et al. 2010). The microwave heating can enhance the early strength and even the long-term strength of cementitious materials (Wu et al., 1987, Hutchison et al., 1991, Sohn and Johnson, 1999, Kong et al., 2016). In addition, the heating method is accompanied by drying. The microwave drying has been proved to be efficiently used in other industries (Guo et al., 2017, Bal et al., 2017, Zhang et al., 2006). With microwave heating, the cementitious materials loses water from the surface due to the temperature rise. But more importantly, the unique volumetric heating may increase the rate of transfer of water from the inner part to the surface and thus increase the rate of drying. From the literature, around 60% of water can be lost from the mortar sample in 60 minutes (Wu et al., 1987). It is expected that the air entrapped in the voids facilitate the migration of water inside the samples. Compared with steam curing, the microwave heating also saves time in the delay time and rate of temperature rise, thus reducing the preconditioning time (Natt Makul, 2011, Makul et al., 2017, Yazıcı et al., 2005, Gonzalez-Corominas et al., 2016).
In summary, microwave heating can be a potentially time-efficient preconditioning method in comparison with the conventionally used method (Shi et al., 2012a, Morshed and Shao, 2014, El-Hassan and Shao, 2014b).

Thus, in this project, the first question raised is ‘whether microwave heating is an efficient preconditioning method for carbonation curing, and if it is, what is the optimum regime?’, the next question is ‘how will the microwave heating as a preconditioning method compare with other preconditioning methods in the literature?’.
3.7 Concluding remarks

In this chapter, the introduction to microwave heating and its application for cementitious materials are reviewed, and also its potential application as a preconditioning method for carbonation curing has been proposed. The following conclusions can be drawn:

- Microwave heating can be used in cementitious materials because of their relatively high dielectric constants. The dielectric constant is especially high when the concrete is in a plastic state.
- Penetration depth increases as the moisture in the concrete decreases. When the concrete is in a plastic state, the penetration depth is only 16 mm but increases rapidly after initial setting, and the penetration depth can reach up to 600 mm at 28d.
- Microwave heating can accelerate hydration of cementitious materials, and thus increase early strength.
- Microwave energy removes considerable amount of water due to its unique volumetric heating nature.
- Microwave heating has the potential to be an efficient preconditioning method for carbonation curing.
Chapter 4 Experimental programme

4.1 Research questions and objectives

The primary aim of this project is to develop a microwave-based preconditioning method, allowing the normally vibrated concrete, which usually contains higher amounts of water than that desired for carbonation curing, to be carbonation cured. It is anticipated that by successfully developing this microwave-based preconditioning technique, this cutting-edge carbonation curing technology can be widely used by the precast industry to effectively improve the early strength of most of the concrete products and, during the meantime, to reduce the carbon footprint of concrete products as well as to mitigate CO₂ emission. To achieve this aim, a detailed experimental design has been developed for this project which is shown in Figure 4.1. As indicated, the whole experimental programme consists of the following three stages:

Stage 1 (Chapter 5): Selection of a suitable microwave-based preconditioning and carbonation curing regime for cementitious materials. In this stage, the effects of main factors in the microwave-based preconditioning and carbonation curing (as identified in Chapter 2) on the compressive strength and carbonation efficiency of the pastes and mortars manufactured with pure PC are studied individually in order to obtain a suitable regime for microwave-based preconditioning and carbonation curing.

Stage 2 (Chapter 6): Evaluation of the effectiveness of microwave heating as a preconditioning method to facilitate carbonation curing. The main focus of this stage is to compare microwave heating with other conventionally used preconditioning methods. The strength development, carbonation efficiency, microstructure and carbonation products of the cement paste and mortar samples were characterised and compared.

Stage 3 (Chapter 7): Investigation into the effects of microwave-based preconditioning on the properties of carbonated PC blends. Three typical
mineral additions, fly ash, GGBS and limestone, were used to study the effect these have on the optimum preconditioning method, and the corresponding strength, carbonation efficiency, microstructure and carbonation products at different ages.
Literature review demonstrates
preconditioning methods are not efficient

Is microwave heating an efficient preconditioning method?

Yes

Question 1: What factors will affect preconditioning and carbonation process on cementitious materials?

Chapter 5

Objective 1

Preconditioning time
(45 min, 70 min, 90 min, 110 min)

Carbonation pressure
(0.5 bar, 1 bar, 5 bar, 5 bar)

Carbonation time
(1 h, 2 h, 4 h, 24 h)

Water distribution

Compressive strength

Degree of carbonation

Microstructure (SEM)

Penetration resistance

carbonation products (XRD/TG)

Chapter 6

Objective 2

Question 2: What are the effects of microwave heating and other preconditioning methods on the preconditioned and carbonated samples

Microwave heating

Air conditioning

Water bath heating

No preconditioning

Temperature and humidity history

Water distribution

Compressive strength

Degree of carbonation

Microstructure (SEM)

Reaction products (XRD/TG)

Chapter 7

Objective 3

Question 3: What are the effects of additions on the microwave preconditioned and carbonated samples

Fly ash

Limestone

GGBS

Determine preconditioning time

Different ages (4h/28d)

Temperature during carbonation curing

Compressive strength

Degree of carbonation

Microstructure (SEM)

carbonation products (XRD/TG)

An efficient preconditioning method is proposed

Figure 4.1 Experimental diagram
4.2 Raw Materials

4.2.1 Portland cement and mineral additions

Portland cement (PC) (CEM I 52.5N, Castle Cement Ltd, UK), complying with BS EN 197-1:2011 (BSI, 2011), was used throughout the experiment. The physical properties and clinker phases of PC are presented in Table 4.1 and Table 4.2. The PC phase contains 4.5% calcium carbonate content from TG analysis.

<table>
<thead>
<tr>
<th>Physical properties of cement</th>
<th>Fineness</th>
<th>410 m²/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial setting time</td>
<td></td>
<td>155 min</td>
</tr>
<tr>
<td>Compressive strength (28 days)</td>
<td></td>
<td>60 MPa</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Clinker phases of the cement (wt/%)</th>
<th>C\textsubscript{3}S</th>
<th>C\textsubscript{2}S</th>
<th>C\textsubscript{3}A</th>
<th>C\textsubscript{4}AF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>62.2</td>
<td>15.8</td>
<td>5.8</td>
<td>7.4</td>
</tr>
</tbody>
</table>

As described in the experimental programme, mineral additions were employed in Stage 3 to further investigate their effects on the threshold preconditioning time, corresponding strength, carbonation efficiency and carbonation products at different ages. Three typical mineral additions were selected, namely, fly ash, GGBS, and limestone powder. Fly ash is a typical pozzolanic addition which can only be activated in an alkaline environment; GGBS can hydrate itself without extra activation but the strength development is very slow compared to PC; limestone powder is normally considered as an inert material in cement hydration at early age though it can react with calcium aluminates in the long term.

In this project, fly ash was supplied by Cemineral Limited in the UK, conforming to the standard BS EN 450-1:2012. Its relative density is 2.25.
GGBS was provided by Hanson UK, in accordance with the standard BS EN 15167:2006. The fineness of GGBS is $527 \text{ m}^2/\text{kg}$, and its relatively density is 2.9.

The limestone powder in this project was provided by Hanson UK, with the majority of particle size less than 10 μm.

The chemical compositions of cement and the mineral additions are shown in Table 4.3. Their CO$_2$ content based on TG analysis will be shown in Chapter 7. The limestone powder is not shown as it is almost pure CaCO$_3$ from the TG analysis.

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Fe$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>62.97</td>
<td>19.37</td>
<td>4.45</td>
<td>0.99</td>
<td>0.19</td>
<td>0.73</td>
<td>2.67</td>
</tr>
<tr>
<td>PFA</td>
<td>2.31</td>
<td>53.08</td>
<td>24.62</td>
<td>1.85</td>
<td>0.08</td>
<td>2.03</td>
<td>10.32</td>
</tr>
<tr>
<td>GGBS</td>
<td>39.4</td>
<td>34.30</td>
<td>15</td>
<td>8</td>
<td>0.40</td>
<td>0.38</td>
<td>0.40</td>
</tr>
</tbody>
</table>

The particle size distribution of the cement is shown in Figure 4.2.
4.2.2 Sand

Standard sand is used throughout the project to reduce variations. The standard sand complies with ISO 679:2009 (IOS, 2009), with the results of sieving test shown in Table 4.4. The water absorption of the standard sand was 1.5%.

<table>
<thead>
<tr>
<th>Square mesh size (mm)</th>
<th>2</th>
<th>1.6</th>
<th>1.0</th>
<th>0.5</th>
<th>0.16</th>
<th>0.08</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cumulative sieve residue (%)</td>
<td>0</td>
<td>7±5</td>
<td>33±5</td>
<td>67±5</td>
<td>87±5</td>
<td>99±5</td>
</tr>
</tbody>
</table>

4.3 Sample preparation

Four types of samples were prepared. For mortar samples, a sand/cement ratio of 2 was applied throughout this project.

(1) Mortar samples with high water/binder ratio (HM). Mortar samples were prepared with a water/binder ratio of 0.37 or 0.5 (0.37 is a normal w/c ratio while 0.5 is a w/c ratio which is the value with slight bleeding). The mixture was based on the sand containing 1.5% water (saturated surface dry). This was designed to test the compressive strength, carbonation efficiency and microstructure of carbonated samples.

(2) Cement paste with high water/cement ratio (HP). In the study, cement paste was used to characterize the reaction products to avoid the influence of sand in the mortar. The water/binder ratio was set as 0.37.

(3) Mortar with low water/cement ratio (LM). Mortar samples were prepared for direct carbonation without preconditioning at a water/cement ratio of 0.15.

(4) Cement paste with low water/cement ratio (LP). Paste samples were prepared for direct carbonation without pre-conditioning at a water/cement ratio of 0.15.
4.3.1 Mixing

**HM and HP:** Samples were mixed with a mortar mixer. The mixing procedures followed the standard BS EN 196-3:2005+A1 2008. Weighed cement, sand, and mineral additions were hand mixed in a plastic container for three minutes. Then water was poured into the mixing bowl followed by the pre-mixed solid powder materials. After mixing for 90 seconds at low speed, the mixer was stopped for 30 seconds during which time the material from the blade, the bottom and wall of the bowl were scraped down and moved back into the middle of the bowl again. Then the mixer was switched on for another 90 seconds at low speed.

**LM and LP:** Cement (or plus sand) and water were weighed and then mixed by hand for 5 minutes in a plastic container (Figure 4.3).

![The paste sample after being mixed by hand](image)

4.3.2 Casting

**HM and HP:** After mixing, HM and HP were cast in moulds. Because the conventional steel moulds are not suitable for microwave heating, polyether
ether ketone (PEEK), a microwave transparent material, was used to make custom-made moulds throughout the project. Two types of moulds were used.

- 25×25×25 mm moulds (Figure 4.4) were used for paste samples.
- 50×50×50 mm moulds (Figure 4.5) were used for mortar samples.

![Figure 4.4 25×25×25 mm moulds](image1)

![Figure 4.5 50×50×50 mm moulds](image2)

The penetration depths of the cement paste and mortar samples used in this project are shown in Figure 4.6. The dielectric properties of the paste and mortar samples were measured by using Agilent Technologies E5071C Network Analyser and Agilent Technologies 85070E dielectric probe kit in UCL. The penetration depth is determined by the dielectric properties and calculated based on Eq.3.2. The figure shows that the penetration depths of the cement paste and mortar increase steadily as hydration proceeds. The values are around 50 mm at the start of hydration, and increase sharply after several hours and finally reach around 160 mm at 24h. The trend is in agreement with the previous studies where the penetration depths of the cement paste and concrete increase with hydration time (Makul, Keangin et al. 2010). The figure also shows that the lowest penetration depth is higher than the size of the mould. In addition, as the hydration proceeds, the penetration depths can further increase.
Figure 4.6 The penetration depth of cement paste and mortar at early time

After casting, the samples were compacted within a mould on a vibration table until few air bubbles were visually seen on the top surface. Then the samples were finished using a steel scraper.

LP: After mixing, LP samples were dispersed on a flat plate, which was to enable sufficient contact of the cement particles with CO$_2$, and cured in a pressure vessel (Figure 4.7).

Figure 4.7 Dispersed cement powder on the plate
LM: LM samples were compacted with a fixed compaction force (8 MPa) for 90 seconds by using a compressive machine (Advantest 9 from Controls). The mould is shown in Figure 8.

![Figure 4.8 Moulds (Ø 31 mm) to compact samples](image)

4.3.3 Preconditioning

After casting was finished, HM and HP samples were kept in moulds and exposed to the preconditioning process, then demoulded before being put in the carbonation chamber. It should be noted that LP and LM do not need such a process. Preconditioning methods include microwave heating (MP), water bath heating (WP) and air preconditioning (AP). It should also be noted that the preconditioning can affect the results of compressive strength because drying has effect on the compressive strength (Burlion et al., 2005, Wang et al., 2017b, Yurtdas et al., 2004). The compressive strengths are higher when the samples are drier. However, this effect is not expected to greatly affect the results of compressive strength in this project because the samples after preconditioning are still mostly wet (before or just after final setting) and far from being completely dry.
4.3.3.1 Microwave heating

Throughout the experiment, microwave heating was applied as a preconditioning method for both mortar and cement paste. The microwave oven used was designed by the AIM Group at University College London and City University of London. The output power of microwave oven can be automatically adjusted according to the feedback of temperature. The temperature is measured by optical fibre sensor which is inserted into the sample.

Figure 4.9 is a diagram of the designed microwave oven and the system which can automatically control the temperature. The sensing interrogator receives the light signals from the sensors and then the signals are converted to electronic signals. The computer software can adjust the output power based on the electronic signals and such adjustment can be applied to the microwave oven via the control unit. The samples are placed symmetrically on a turntable, which rotates clockwise and anticlockwise to avoid the fibres becoming twisted.

- Microwave heating for **mortar samples (HM)**. The temperature was increased from ambient to 70°C in 15 minutes, then held at this temperature until the end of the experiment.
- Microwave heating for **cement paste samples (HP)**. The temperature was increased from ambient to 70°C in 30 minutes, then held at this temperature until the end of the experiment.

![Diagram of the custom-made microwave oven](image)

**Figure 4.9 The diagram of the custom-made microwave oven**
4.3.3.2 Water bath heating

In Stage 2, other preconditioning methods were compared with microwave heating. The water bath chamber is shown in Figure 4.10. The samples in the water bath chamber were sealed with 3 layers of cling film to avoid water evaporation before being put in a sample bag and immersed in water. Samples were placed on top of a plastic cone to avoid direct contact with the bottom of the chamber. The samples were supported to the same height of the water inside the chamber.

- Water bath heating for mortar samples (HM). The temperature of the mortar sample was controlled to be close to the temperature of sample subjected to microwave heating, as seen in Chapter 6. This is achieved by putting the samples in the water bath chamber with the temperature of water maintained at 70°C.

- Water bath heating for cement paste samples (HP). The temperature of the paste sample was controlled to be close to the temperature of sample subjected to microwave heating. This was achieved by putting the paste sample in the chamber, with the temperature of water inside the chamber increasing from ambient temperature to 70°C in 30 minutes.
4.3.3.3 Air preconditioning

For the air preconditioning (AP) process, the samples were put in a curing room, where the temperature and humidity of the room were maintained at 20°C and RH 50%±5%.

In this study, after mixing and casting, samples were kept in the mould and placed in the curing room for 5 hours (exposure to air). The samples were then demoulded and put back in the curing room for another 19 hours (exposure to air). The amount of water loss in the total 24 hour process was similar to that in the microwave preconditioned samples.

4.3.4 Carbonation curing

After preconditioning, the samples were demoulded and then exposed to carbonation curing in a pressure vessel. The diagram of the pressure vessel is shown in Figure 4.11.

At the start of carbonation curing, the inlet valve was opened and then the outlet of the valve was opened for 40 seconds to allow CO₂ to flush air out of the
chamber. The outlet of the valve was then closed. The pressure of the gas can be read from the pressure gauge.

After the curing process was finished, the inlet valve was closed first, and then the outlet of the valve was opened to release gas from inside the chamber.

In a parallel experiment, the reference samples without carbonation were put in a curing room with the temperature 20°C and RH 50%±5%.

![Diagram of the carbonation curing system](image)

Figure 4.11 The scheme of carbonation curing system

### 4.3.5 Further curing

After curing in CO₂ or in the air for a specific period, some of the mortar or paste samples were tested immediately, while the rest were wrapped with wet cloth in a sealed bag and placed in the curing room (20°C) and tested at different ages.
4.4 Test method

4.4.1 Tests during the preconditioning process

4.4.1.1 Temperature during preconditioning

The temperature sensor with three gratings was inserted into the mortar samples at different depths (12.5, 25 and 37.5 mm) to measure the temperature during the heating process. The positions of the optical fibre and gratings are shown in Figure 4.12. T1, T2 and T3 were used to measure the temperatures of the top, core and bottom of the sample. The photo of the optical fibre is shown in Figure 4.13. For the paste sample, a temperature sensor with only one grating was inserted into the paste sample to measure the temperature during the heating process.

4.4.1.2 Relative Humidity (RH) during preconditioning

An optical fibre humidity sensor was placed 5 cm above the sample in the microwave chamber. The relative humidity (RH) was monitored continuously during the microwave heating process. During the water bath heating, the RH was expected to be at 100% as the samples were well sealed by 3 layer of films before being put into the sample bag. The air in the sample bag is then excluded.
4.4.1.3 Water loss before carbonation curing

Water is added to a sample at the mixing process, and then evolves to other types of water during the preconditioning process: namely, water evaporated during heating (evaporated water 1), water evaporated after heating but prior to carbonation curing due to the temperature difference between the sample and environment (evaporated water 2), water combined in the chemical hydration reaction (combined water) and remaining free water.

Evaporated water 1 is expressed as the ratio of the mass change before and after preconditioning to the total water added, as shown in Eq. 4.1.

\[
\text{Evaporated water 1} \, (\%) = \frac{\text{Mass}_{\text{after}} - \text{Mass}_{\text{before}}}{\text{Mass}_{\text{water}}} \quad (4.1)
\]

where \( \text{Mass}_{\text{after}} \) refers to the mass of samples after preconditioning, \( \text{Mass}_{\text{before}} \) refers to the mass of samples before preconditioning, and \( \text{Mass}_{\text{water}} \) refers to the mass of water initially added.

Evaporated water 2 is expressed as the ratio of the mass change immediately after demoulding and before the start of carbonation to the total water added, as shown in Eq. 4.2. The water loss is mainly due to the higher temperature in the sample than that in the surrounding environment and the time between the two processes is controlled to be 20 min.

\[
\text{Evaporated water 1} \, (\%) = \frac{\text{Mass}_{\text{sample}} - \text{Mass}_{\text{after}}}{\text{Mass}_{\text{water}}} \quad (4.2)
\]

where \( \text{Mass}_{\text{sample}} \) refers to the mass of samples just before carbonation.

Combined water is the ratio of the mass of water combined to the total water added and is determined by TG (see Section 4.4.5.2), as percent of mass loss.
between 105°C to 500°C, and then normalized to the ratio of mass loss to the total water content.

The remaining free water is obtained from the Eq. 4.3 as below.

\[
\text{remaining water (\%)} = 100\% - \text{evaporated water 1(\%)} - \text{evaporated water 2 (\%)} - \text{combined water (\%)}
\]  
(4.3)

4.4.1.4 Penetration resistance

After preconditioning, the penetration resistance was measured following ASTM C403 (ASTM, 2008). Needles of standard sizes are inserted into the mortar to a specific depth, and the force required to reach the penetration depth was measured, from which, the penetration resistance of the mortar can be calculated. A penetration resistance of 3.5 MPa and 27.6 MPa are described as the initial and final setting times. Throughout the project, the size of mortar samples was fixed at 50 mm cubes.

4.4.2 Tests during the carbonation curing process

After preconditioning, a thermocouple was inserted into the samples (a hole was prepared before hardening) to monitor the temperature of samples (at a depth of 10 mm) during the carbonation curing process (Figure 4.14). The data were collected every second using a TC-08 thermocouple data logger (Pico technology, UK).
4.4.3 Tests on hardened samples

The following tests were conducted on mortar samples only.

4.4.3.1 Compressive strength

Samples were tested with a compressive machine (Advantest 9 from Controls), with a loading rate of 500 N/s. At least three samples were measured in each test and the results averaged.

4.4.3.2 Phenolphthalein test

Samples were split into half from the top to the bottom, and phenolphthalein solution was sprayed on the fracture section to map the carbonation depth. The solution was made by dissolving 1g phenolphthalein in 70 ml ethyl alcohol and diluted to 100 ml with deionized water, in accordance with the British standard (BSI, 2006).
4.4.3.3 CO$_2$ uptake

The CO$_2$ uptake was measured by assuming all CO$_2$ absorbed during carbonation curing process was lost over the temperature range of 500°C ~ 1000°C. The process of sample preparation is as follows.

(1) After crushing, the broken samples were further split into small pieces using a hammer.

(2) The weight of a crucible was measured to be W1.

(3) Then the small pieces of sample were put in the crucible.

(4) The crucible and sample were placed in a furnace and heated from room temperature to 500°C in 30 minutes and kept at 500°C for 2h. Then the crucible and sample were removed and exposed to the air to cool down for 20 minutes, and then moved to a desiccator to further cool down to ambient temperature. Then the weight was measured again and designated to be W2.

(5) The crucible and sample were put in the furnace again and heated from room temperature to 1000°C in 60 minutes and kept at 1000°C for 2h. On removal from the furnace, the crucible and sample were exposed to the air to cool down for 30 minutes, and then moved to a desiccator to further cool down to ambient temperature, to give the measured weight, W3.

(6) CO$_2$ uptake was calculated using the Eq. 4.4.

\[
\text{CO}_2\text{ uptake} = \frac{w_2 - w_3}{(w_3 - w_1)\times \alpha} - w_4
\]  

(4.4)

Where $\alpha$ is the percentage of cement added in the solids; $w_4$ is the weight loss of cement from 500°C to 1000°C.

4.4.4 Sample preparation for phase analysis and microstructure test

**HM**: Samples were drilled with a drilling machine to obtain powder samples of specified depth ± 0.01 mm.
Mortar samples fragments were preserved for examination by SEM (see Section 4.4.6.1). The top 0-10 mm layer and the top 25-35 mm layer were kept and further broken down into small pieces by using pliers.

For BSE tests, after the mortar samples were dried using the drying method described below, the samples were impregnated with an epoxy resin and polished. The samples were then carbon coated and examined by SEM (see Section 4.4.6.1).

**HP:** Carbonation products were characterised on powder samples of paste by XRD and TG. The phenolphthalein test showed the carbonation depth of a carbonated cement paste was around 6-8 mm. To study the highly carbonated and the semi-carbonated phases, depths of 0-2 mm and 6-8 mm were selected for all paste samples. Then the collected powder was dried in the method below and held for further analysis.

**LM:** The mortar sample was crushed after carbonation, and the top layer close to the surface was collected and dried in the described method before SEM was conducted. In addition, some dried pieces of the top layer were impregnated with the epoxy resin and polished for BSE measurements.

**LP:** The paste sample was dried with the following drying method, and prepared for XRD and TG analysis.

**Drying:** After the powder or fragments were obtained, those samples were put in acetone for three days to arrest further hydration. The samples were then dried in a desiccator with silica gel and constant vacuum for another three days.

Cement paste samples were prepared for XRD and TG analysis, and they were ground with a mortar and pestle to pass 63 μm sieve.
4.4.5 Phase analysis

4.4.5.1 X-ray Powder Diffraction (XRD)

XRD is a technique to determine the atomic and molecular structures of crystalline materials. A beam of X-rays diffract due to the crystal structures of the materials and the diffracted waves are then received by a detector. The received signals can be converted to XRD patterns with different peak positions and intensities. Therefore, the XRD technique can be used to detect the crystalline phases in an unknown material. In this project, XRD is used to detect the cement components, its hydrates and carbonation products, such as C$_3$S, C$_2$S, CH, AFT and CaCO$_3$.

Powder samples were analysed with a Bruker AXS D8-Advance automated X-ray diffractometer using Cu Kα radiation at 40 kV and 250 mA. The test was performed over a 7° ~ 70° range with 8° (2θ) per minute.
4.4.5.2 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) is a useful tool that measures the changes of sample weight both qualitatively and quantitatively. When cement hydrates and carbonation products undergo thermal reactions, they are associated with weight losses. The weight losses and the related temperature are recorded by the TGA instruments. In this case, the types and quantity of the reaction products formed during hydration and carbonation can be identified and calculated. In this project, the technique can be used to quantitatively calculate the amount of CH and crystalline CaCO$_3$, which can also be identified in XRD test. In addition, this technique can also be used to identify the presence and amount of C-S-H gel and amorphous CaCO$_3$, which cannot be identified in XRD test.

The apparatus used was a TG 209 F1 Libra supplied by Netzsch Company in Germany, heating from ambient temperature to 1000°C at a rate of temperature increase at 10°C/min, under an atmosphere of flowing nitrogen gas.
4.4.6 Microstructure test (SEM)

The SEM instrument produces a beam of electrons which collide with the samples and these electrons are bound off or produce new electrons which are then received by different detectors. There are three types of electrons which are most important in this project. The first type is secondary electrons (SEs). The SEs are knocked out from the atoms of the materials when the incoming electrons collide with the samples. The brightness of the SEs are determined by the inclination angle of the surface, and thus they are commonly used to detect the morphology of samples. The second type is backscattered electrons (BSE). When the incoming electrons collide with the atoms of samples, they bound off before being received. The brightness of the BSE are determined by the atomic number of the atoms in the samples. Therefore, the BSE can reflect different compositions in the images. The samples are commonly polished to avoid the influence of topography. The third type is characteristic X-rays. They are emitted when the electrons from the outer shell of the molecules of samples fall into the inner shell, so they can be used to characterise the elements of samples.

Freshly fractured mortar was coated with gold, and put in a FEI QUANTA 250G SEM instrument, in order to measure its morphology by detecting SEs. Some polished samples were coated with carbon, and also put in the same instrument in order to obtain compositional distribution by measuring BSEs. Energy dispersive spectroscopy (EDS) was performed using an OXFORD X-MAX instrument.
Chapter 5  Development of a suitable protocol for microwave-based preconditioning and accelerated carbonation curing

5.1 Introduction

Based on the literature review in Chapter 3, microwave heating has been identified and, therefore, proposed as a potential alternative preconditioning method for the accelerated carbonation curing in the current study. It is anticipated that due to its thermal effect, microwave heating could remove water (either physically by evaporation or chemically by enhanced hydration) more efficiently compared to conventional preconditioning method and, thus, could be able to facilitate the subsequent carbonation curing. On the other hand, as discussed in Chapter 2, the non-thermal effect of microwave could also contribute to the hydration and carbonation curing process. From the literature review in Chapter 2, three factors, namely, preconditioning time, carbonation time and CO₂ pressure have been identified as the most influential factors affecting the preconditioning and carbonation curing. The effects of these three factors on the properties and reaction products of the plain PC mortar and paste samples as well as their effect on the carbonation efficiency were studied separately and are reported in detail in this Chapter in an attempt to establish a suitable protocol for the proposed microwave-based preconditioning and subsequent accelerated carbonation curing.

5.2 Aim and objectives

The overall aim of this chapter is to establish a suitable regime for the microwave-based preconditioning and subsequent carbonation curing. This was achieved through the following objectives:

Objective 1: To investigate the effects of microwave-based preconditioning time on the compressive strength development and carbonation efficiency of the carbonation cured plain PC mortar, in order to determine the effect that the
microwave-based preconditioning time may have on the subsequent carbonation curing.

**Objective 2:** To study the effects of carbonation time and \( \text{CO}_2 \) pressure on the compressive strength development, carbonation efficiency, microstructure and reaction products of the carbonation cured plain PC mortar and cement paste in order to determine the most suitable carbonation time and \( \text{CO}_2 \) pressure for the accelerated carbonation curing.

### 5.3 Effects of microwave-based preconditioning time on the properties of plain PC mortar

#### 5.3.1 Introduction

From the literature review in Chapter 2, the transport of \( \text{CO}_2 \) has been identified as the most influential factor for increasing the carbonation efficiency. The rate of transport of \( \text{CO}_2 \) is determined by the free water content, the permeability of the cementitious material and the pressure of \( \text{CO}_2 \) (Fernandez Bertos et al., 2004). Previous research with different preconditioning methods have shown that, with a set temperature history, the free water content is decided by preconditioning time (Shi et al., 2012a, Morshed and Shao, 2014, Tu et al., 2018). Moreover, the permeability of cementitious materials is also decided by the preconditioning time due to its influence on the degree of hydration and the moisture content of the matrix (Neville, 2011). Therefore, it can be deduced that the microwave-based preconditioning time could affect both the remaining water content and the permeability of cementitious materials.

In this section, the effects of microwave-based preconditioning time on the compressive strength and carbonation efficiency of carbonation cured plain PC mortars were, thus, studied in detail.
5.3.2 Selection of the parameters in the preconditioning process

Temperature and the duration of the preconditioning have been identified as the most important parameters which must be carefully controlled in order to reach the optimum conditions for carbonation curing (Morshed and Shao, 2014, Tu et al., 2018). To develop a microwave-based preconditioning technique, these two parameters should also be carefully considered and this has been further elaborated below.

5.3.2.1 Temperature profile

Before the proposed microwave-based preconditioning is applied, it is essential to identify the temperature profile to be used in the microwave heating process. As discussed in Chapter 3, the advantages of microwave heating include precise control of temperature, rapid temperature increase and a high rate of drying (Mujumdar, 2006, Kaewwichit et al., 2017, Guo et al., 2017, Bal et al., 2017, Bal et al., 2010).

It is generally accepted that an increase in temperature leads to a higher rate of drying, but heating above 70°C may cause the delayed ettringite formation (DEF) of PC-based materials and thus damage the long-term strength of the cementitious materials (Asamoto et al., 2017, Amine et al., 2017, Taylor et al., 2001). Therefore, the temperature used in this project was selected as 70°C to avoid the occurrence of DEF. Unlike steam curing, the rate of temperature increase from microwave heating can be much higher as discussed in Chapter 3 (Leung and Pheeraphan, 1997, Sohn and Johnson, 1999). In this project, the rate of temperature increase was set at 3°C/min based on some preliminary trials. This rate can lead to the increase of the temperature of the mortar samples to be studied from the ambient temperature to 70°C within 15 mins. The temperature was then held at 70°C until the end of preconditioning period.
5.3.2.2 Preconditioning time

With a longer preconditioning time, both the amount of water evaporated and the degree of cement hydration can increase. Water evaporation benefits the rate of transport of CO$_2$; however, the higher degree of cement hydration reduces the rate of transport of CO$_2$. So ideally, the optimum preconditioning time will be when the remaining free water is appropriate for the carbonation reaction but the permeability of the mortar is still high enough to enable the transport of CO$_2$.

In this study, the samples need to be demoulded before the subsequent carbonation curing to ensure all the six sides of the samples are exposed to CO$_2$. Therefore, at least initial setting is required before the samples can be demoulded. Previous studies showed microwave heating for around 45 min was beneficial to the later strength development of cementitious materials (Natt Makul, 2011, Leung and Pheeraphan, 1997). Preliminary experiment also showed that 45 min preconditioning was sufficient for demould. Thus 45 min was selected as the starting point in this project. After that, 70 min, 90 min and 110 min were used to compare the effects of preconditioning times on carbonation efficiency. Preconditioning times beyond 110 min were not studied. This is mainly because the preliminary trials showed that when the preconditioning time is above 70 min, only minor changes in compressive strength and CO$_2$ uptake were observed after carbonation curing. Another reason is that a longer preconditioning time increases the degree of hydration, and thus reduces the permeability of mortar samples and the subsequent CO$_2$ transport.

Therefore, preconditioning times of 45 min, 70 min, 90 min and 110 min were selected to study their effects on the cementitious materials subjected to subsequent carbonation curing.
5.3.3 Effects of preconditioning time on the water distribution of mortar before carbonation curing

The water added initially can be considered as free water, but after preconditioning it is converted to other types of water, namely, evaporated water 1 (water evaporated during heating), evaporated water 2 (water evaporated after heating but prior to carbonation curing), combined water (water combined in the chemical hydration reaction) and remaining free water. To facilitate the following discussion, shorthand notations are used to refer to the mortar samples with different w/c ratios, i.e. M0.37 for w/c ratio of 0.37 and M0.50 for w/c ratio of 0.5.

Figure 5.1 shows a typical water distribution of M0.37 and M0.50 after preconditioning for 70 min. It should be noted that before carbonation curing, the evaporated water 1 and evaporated water 2 have been lost and are not contained in the samples. After M0.37 had been subjected to 70 min preconditioning, the remaining free water made up most of the water (61.5%), followed by evaporated water 1 (20.1%) and evaporated water 2 (10.6%), respectively. The smallest proportion was the combined water (7.8%). In comparison to M0.37, Figure 5.1(b) shows that the free water content in M0.50 was lower (57.3%) accompanied by a higher proportion of evaporated water 1 (25.1%), and similar proportions of evaporated water 2 (10.7%) and combined water (6.9%).

Interestingly, more evaporated water 1 (25.1% vs. 20.1%) was lost from M0.50 than for M0.37. This is consistent with the previous study by Rattanadecho et al. (2008) in which the cement paste of different w/c ratios were subjected to a fixed microwave energy of 800 W, and the water was lost faster from the samples with a high w/c ratio. One possible explanation could be that M0.50 contains more water and, hence, is much easier to absorb microwave energy due to its better dielectric properties than the other constituent materials, making it easier to lose water. Another explanation could be that the microstructure of M0.50 was more loosely formed due to its high w/c ratio, at
least initially, which allows easier migration of water from the interior to the surface, thus increasing the water loss (Roca et al., 2008, Yang et al., 2017).

Figure 5.1 Water distribution of mortar preconditioned in microwave oven for 70 min
The changes in the contents of four types of water in the M0.37 and M0.50 at different preconditioning times are presented in Figure 5.2. A similar trend was observed from both samples: evaporated water 1 and combined water increased steadily and the evaporated water 2 decreased with preconditioning time. The overall changes in these three types of water resulted in a constant decrease in the remaining free water. M0.37 exhibited a free water content of 72.9% at 45 min and this was reduced to 51.1% at 110 min (Figure 5.2 (a)). The remaining free water content at all time points was slightly lower in M0.50 than its corresponding counterpart in M0.37. It is worth noticing that 64% was recorded at 45 min and this was reduced to 47.9% at 110 min (Figure 5.2 (b)).
Figure 5.2 Water distribution of mortar with two different w/c ratios preconditioned in microwave oven for different duration
5.3.4 Effects of preconditioning time on the compressive strength of mortar after carbonation curing

In this study, three groups of samples were studied to show the influence of carbonation curing, namely, the sample immediately after preconditioning, the sample after preconditioning and 2h hydration, and the sample after preconditioning and 2h carbonation. The effects of preconditioning time on the compressive strength of the M0.37 mortar are shown in Figure 5.3 (a). It can be seen that the mortar sample subjected to the initial microwave-preconditioning followed by a 2h-carbonation curing exhibited the highest strength among all the three groups. In particular, the strength increase between 45 mins and 70 mins was significant, with a value of 9.6 MPa obtained at 45 min whilst 27.6 MPa was reached at 70 min. Surprisingly, little strength gain was noticed from 70 mins to 110 mins preconditioning. This agrees well with a study by Shi et al. (2012a) where there was little development in carbonated strength after the threshold preconditioning time, but the study did not attribute this to a specific reason. It should be noted that the samples immediately after preconditioning showed a relatively low strength. For example, only 2.7 MPa was reached at 90 min and 7.4 MPa at 110 min. Even with another 2h hydration, the strength increase was still marginal. The above results clearly demonstrated the significant contribution of carbonation curing to the strength development of the PC mortar. Additionally, it seems that there is a threshold preconditioning time needed for the optimum carbonation curing. Once this threshold preconditioning time is reached, the effect of preconditioning time on the strength development of carbonation cured PC mortar is insignificant. The possible reason behind this observation is further elaborated in Section 5.3.5 below.

Similar results were observed from the M0.50 mortar samples and these are shown in Figure 5.3(b). However, in contrast to M0.37, the compressive strength of M0.50 immediately after preconditioning was barely measurable. Consequently, the value immediately after preconditioning is not shown in Figure 5.3 (b). Nonetheless, the samples after 2h carbonation curing show a higher strength than those with only hydration. Although the compressive strength after carbonation curing was relatively low at 45 min and 70 min (with
1.3 MPa and 4.9 MPa being measured respectively), this was rapidly increased to 15.8 MPa at 90 min. However, even after another 20 min preconditioning, the compressive strength remained the same. This pattern is much similar to that in M0.37 where after certain preconditioning time, there is no significant increase in strength after carbonation. Based on the current results, these threshold preconditioning times were 70 min and 90 min for M0.37 and M0.50, respectively.
Figure 5.3 Effects of preconditioning time on compressive strength with and without carbonation
5.3.5 Effects of preconditioning time on the CO$_2$ uptake and carbonation profile

The CO$_2$ uptake and the carbonation depth are two important parameters used to assess the carbonation efficiency of carbonation curing (Zhan et al., 2013, Mo et al., 2016). Figure 5.4 shows the CO$_2$ uptake of mortar samples subjected to different microwave preconditioning times followed by a 2-h carbonation curing. The M0.37 sample (w/c ratio of 0.37) preconditioned for 45 min exhibited the least CO$_2$ uptake (5.94%), however, this was increased rapidly to 10.9% at 70 min. Longer preconditioning times of 90 min and 110 min did not further increase the CO$_2$ uptake. The M0.50 sample (w/c ratio of 0.5) also showed that an initial increase in preconditioning time from 45 min to 70 min then to 90 min greatly increased the CO$_2$ uptake from 5.99% to 9.8% then to 13.9%, but a preconditioning time for 110 min did not further increase the CO$_2$ uptake. This pattern is similar to the compressive strength results presented in Figure 5.4.

![Figure 5.4 Effects of preconditioning time on CO$_2$ uptake](image)

Phenolphthalein spray was used to measure the carbonation depth of mortar samples. The colour of phenolphthalein turns red when in contact with alkalis,
so the colourless part of the fracture surface of specimens can be regarded as the carbonated area. The carbonation profiles of the M0.37 mortar samples subjected to different preconditioning times followed by 2h carbonation curing are presented in Figure 5.5 (a). The least carbonation depth was found in the sample preconditioned for 45 min, but was significantly higher when preconditioned for 70 min. However, after 70 min, no significant changes were observed in the carbonation profiles with preconditioning times 90 min and 110 min.

Figure 5.5 (b) shows the carbonation profiles of the M0.50 mortar samples subjected to different preconditioning times and 2h carbonation curing. The mortar samples showed a steady increase in the carbonation depth when preconditioned from 45 min to 90 min. With a preconditioning time of 110 min, the carbonation depth did not progress further.

The results for compressive strengths and CO₂ uptake as well as carbonation depth all show a threshold preconditioning time. For a w/c ratio of 0.37 this time is 70 min, while for w/c ratio 0.5 it is 90 mins.

The existence of a possible threshold preconditioning time might be due to the following reasons. At the beginning of the preconditioning, the top surface of the sample is saturated with water, which impedes the transport of CO₂ (Tu et al., 2018, Sharma and Goyal, 2018, Seo et al., 2018b, Guo et al., 2018, Zhang et al., 2017). As the water is gradually lost from the top layer, CO₂ diffuses into the mortar, leading to the increase in both the carbonation depth and CO₂ uptake. The top layer then becomes less permeable due to the formation of expansive carbonation reaction products which, consequently, reduces the transport of CO₂ to deeper layer (Zhang and Panesar, 2018a, Zhang and Shao, 2018). As a result, once the threshold preconditioning time is reached, the deep layer is hard to be carbonated. Therefore, the threshold time occurs once water content in the top layer is appropriate for carbonation, but with further carbonation, the carbonation cannot proceed any further.
Figure 5.5 Effect of preconditioning time on the carbonation profiles of the specimens (M0.37 and M0.50)
5.3.6 Discussion

A longer preconditioning time generally leads to a higher amount of water loss, and thus facilitates the subsequent transport of CO$_2$ (Shi et al., 2012a, Morshed and Shao, 2014, Tu et al., 2018). In this project, microwave-based preconditioning is used prior to carbonation curing to study its effect on the subsequent carbonation curing.

Microwave heating evaporates a significant amount of water after a relatively short period of preconditioning. In this study, the threshold preconditioning time varied for different w/c ratios and for M0.37 and M0.50 were 70 min and 90 min, respectively. At the above preconditioning time, the water loss (evaporated water 1 and evaporated water 2) for M0.37 was 30.7% and for M0.50 was 35.8%, respectively. This rate of water loss is considerably higher than that found in the conventional preconditioning methods (Rostami et al., 2012a, Zhang and Shao, 2016a). For example, Rotami et al. (2012a) cast the cement paste samples (w/c ratio of 0.36) by vibration and then the paste specimens were preconditioned in an environmental chamber for 18h at 60% R.H. and 25°C for 20h. Around 40% of the initially added water was lost during this preconditioning process. In another study, Zhang and Shao (2016) cast concrete specimens (w/c ratio of 0.4) by vibration, and then the specimens were preconditioned in-mould to reach initial set (25°C and RH 60%) for 5h and then demoulded and subjected to ambient conditioning (25°C and RH 50%) at a wind speed of 1m/s for 6.5h. Around 40% of the added water was lost from these samples during preconditioning. Compared to these data from literature, it becomes evident that a much shorter preconditioning time is needed from microwave heating for sufficient preconditioning, indicating microwave heating is a more time-efficient heating method for preconditioning process prior to carbonation curing. The enhanced preconditioning from microwave as compared to conventional preconditioning can be mainly attributed to the extra heat that the microwave brings to the samples. Compared with the conventional preconditioning methods, such as exposure to lower humidity and fan drying (Rostami et al., 2012a, Zhang and Shao, 2016a), microwave heating can speed
up the moisture from the surface to the environment (Al-Duri and McIntyre, 1992) and the migration of water within the specimens microwave heating, due to its unique volumetric heating mechanism (Zhang et al., 2006). Furthermore, compared to the conventional preconditioning methods reported in the literature where long preconditioning times were used (and, hence, the microstructure could have been well formed) (Zhang and Panesar, 2018a, Tu et al., 2018, Sharma and Goyal, 2018, Zhang and Shao, 2016a), the microstructure of microwave-preconditioned matrices is reasonably porous due to the short preconditioning time. This loosely formed structure could be another reason that contributes to the increased drying rate, as the porous structure can facilitate the transfer of moisture from inside of the samples (Roca et al., 2006, Roca et al., 2008, Yang et al., 2017, Baik and Marcotte, 2003).

It is generally agreed in the previous studies that there is an optimum water loss in the preconditioning process for subsequent carbonation curing (Shi et al., 2012a, Shi and Wu, 2008), but the optimum water loss was not universally the same among different studies. Shi et al. (2012a) studied the effect of preconditioning on lightweight concrete (size of Ø 100×100 mm) moulded by compaction (w/c ratio of 0.43 ~ 0.5), with the optimum water loss to be 4.5%. Morshed and Shao (2014) investigated the effect of the amount of water loss on the concrete (size of 127×76× 40 mm) at two initial w/c ratios (0.25 and 0.4), moulded by vibration compaction, and found around 42% for an initial w/c ratio of 0.25 and 52% for an initial w/c ratio of 0.4. In another study by Tu et al. (2018), the concrete (initial w/c ratio of 0.35) was prepared by compaction. It was found that around 25% water loss was the optimum for pure cement concrete (size of Ø50×150 mm). The reason for these variations could be that the specimens had different specimen sizes and that within the specimens, the water distribution was different.

In the current study, the mortar samples were moulded by vibration rather than compaction. Therefore, more water on the surface needs to be evaporated to increase the transport of CO₂. This further shows that the water loss cannot be used as the indicator for the threshold preconditioning time in the samples.
subjected to microwave heating. The final setting times may be a more direct indicator for the threshold preconditioning time in this study.

Penetration resistance was used to determine the setting time of mortars. The penetration resistance values of 3.5 MPa and 27.6 MPa are related to initial setting and final setting, respectively (ASTM, 2008). Figure 5.6 shows the changes of penetration resistance of M0.37 (w/c ratio: 0.37) and M0.50 (w/c ratio: 0.5) after different preconditioning times. Both samples demonstrated a significant increase in penetration resistance between 30 min and 110 min. For M0.37, the penetration resistance was barely measurable with preconditioning for 30 min, and slightly increased to 1.19 MPa at 45 min, well below the value corresponding to the initial setting (3.5 MPa). The penetration resistance developed rapidly afterwards, with a value of 16.68 MPa recorded at 60 min and 25.02 MPa at 70 min, just under the value corresponding to the final setting. Lower penetration resistance was observed for M0.50, with a value of 3.32 MPa recorded at 70 min (below initial setting), but this rapidly increased to 33.36 MPa (beyond final setting) at 90 min. It should be noted that penetration resistance is out of range shortly after the final setting time. The results show that the final setting time for samples with both w/c ratios is very close to the threshold preconditioning time.
The reasons can be explained as follows. To facilitate the transport of CO$_2$, the capillary pores need to be unsaturated, and an internal relative humidity of 50% ~ 60% is considered to be the threshold for normal carbonation and carbonation curing (Neville, 2011, Galan et al., 2013). For the current preconditioning methods where most water is lost after final setting (Tu et al., 2018, Sharma and Goyal, 2018, Seo et al., 2018b, Guo et al., 2018, Zhang et al., 2017), water is gradually lost from the capillary pores, and increases the transport of CO$_2$.

Generally setting is referred to as the change from a fluid to a rigid state with barely measurable strength (H.F.W.Taylor, 1997, Neville, 2011). The framework have not been formed before initial set, and the framework starts to form from a plastic network of cement particles during initial set and final set (Neville, 2011). The voids which are initially water become capillary pores. After set, the gross volumes then remain generally unchanged. In this study, most of the water is lost at a very early stage (before final setting) during microwaving. With the high workability of the fresh mortar, the capillary pores collapse due to the evaporation of water (before initial setting) which impedes the transport of CO$_2$. This is similar to the vacuum dewatering process which reduces water content.
at early stage in a way that densifies the concrete structure (Şimşek, 2005, 
Hatanaka et al., 2007). The densification effect was also observed in the 
microwave heating of concrete at an early stage (Wu et al., 1987, Hutchison et 
al., 1991, Makul et al., 2017). At this stage, it is expected that the loss of water 
would not readily facilitate subsequent CO$_2$ curing due to the densification of the 
structure. But when the structure is formed between initial setting and final 
setting, the capillary pores remain open after the removal of water and thus the 
loss of water from the capillary pores then facilitates the subsequent transport of 
CO$_2$. As a consequence, the threshold preconditioning time is close to the final 
setting time.

In summary, microwave-based preconditioning provides an efficient 
preconditioning method. For each mortar with different w/c ratios, there is a 
threshold preconditioning time, after which the compressive strength and 
carbonation efficiency after carbonation curing do not change significantly. In 
addition, the threshold preconditioning time is close to the final setting time.
5.4 Effects of carbonation time on properties of mortar and related carbonation products

5.4.1 Introduction

The literature review in Chapter 2 highlighted that carbonation time may influence the extent of transport of CO$_2$ and, hence, the carbonation products. Microwave heating is a potential new preconditioning method with a different heating mechanism when compared to the current preconditioning methods (Zhang et al., 2017, Pan et al., 2017, Rostami et al., 2011). For example, in the current study, it has demonstrated that sufficient preconditioning can be achieved within 70 minutes of microwave-based preconditioning, which, compared to the 6-18 hours needed for the conventional preconditioning, is more efficient and time-saving. The porosity of the cementitious materials could be higher and the degree of hydration of samples could be lower under microwave heating due to this short preconditioning time. As a result, it may affect the subsequent CO$_2$ transport and the products formed from carbonation curing. Therefore, the carbonation time needed for the microwave preconditioned cementitious materials to obtain the optimum performance from carbonation curing is, thus, uncertain, which could be different from those established from the conventional preconditioning methods. Therefore, in this section, the effects of carbonation time on the compressive strength, carbonation efficiency, microstructure and carbonation products of the plain PC-based matrices were studied after the microwave-based preconditioning.

As explained in Section 4.3, both the mortar and paste samples were employed in this section so that not only the mechanical properties and CO$_2$ uptake could be investigated, but the reaction products and the microstructure could also be examined in detail. The exact arrangements of the PC samples are as follows. The mortar samples were used to investigate the effect of carbonation time on the compressive strength, CO$_2$ uptake and carbonation depth of the microwave-preconditioned PC system in Section 5.4.3, whilst In Section 5.4.4, the microstructure of mortar subjected to different carbonation times is assessed with SEM and BSE-SEM. Then in Section 5.4.5, paste samples were prepared
to characterize the carbonation products of the highly carbonated and semi-carbonated layers of the paste using XRD and TG.

5.4.2 Experimental design

The mortars with w/c ratio of 0.37 were prepared and then subjected to microwave-based preconditioning for 70 min. After that, the mortar samples were put in the CO\textsubscript{2} chamber at 5 bar CO\textsubscript{2} pressure for different durations (1h, 2h, 4h and 24h). To study the effects of carbonation curing time on strength, a parallel experiment with the samples subjected to normal hydration was conducted. In addition, cement paste with w/c ratio of 0.37 was also prepared to study the effects of carbonation time on the reaction products.
5.4.3 Effects of carbonation time on the properties of mortar

5.4.3.1 Effects of carbonation time on the compressive strength of mortar

The compressive strengths of the preconditioned mortar samples following hydration or carbonation curing are shown in Figure 5.7. The mortar samples both cured with hydration only and with carbonation curing, showed significant increase in strength between 1h and 24h. However, the carbonated mortars exhibited much higher compressive strengths than the samples simply allowed to hydrate. The compressive strength after carbonation curing increased from 14.02 MPa at 1h to 27.59 MPa at 2h, but with further carbonation for another 2 hours, the rate of increase was lower, with only 33 MPa reached at 4h. Nonetheless, after 24h carbonation curing, the compressive strength continued to increase, reaching the highest strength of 53 MPa. A reasonable increase in compressive strength was also observed in the samples with normal hydration only, increasing from 3.42 MPa at 1h to 6.72 MPa at 2h, then to 15 MPa at 24h. The difference of the compressive strengths between the samples cured by carbonation curing and normally hydration can be attributed to the contribution of carbonation curing.

Figure 5.7 Compressive strength of mortar with and without carbonation
5.4.3.2 Effects of carbonation time on CO₂ uptake and carbonation profile

Figure 5.8 shows the progress of CO₂ uptake of the mortar with different carbonation times from 1h to 24h. The CO₂ uptake increased continuously with longer carbonation times, initially increasing rapidly with 7.4% reached at 1h and 10.9% at 2 h. After that, the rate of increase was lower, with 14.4% at 4 h and 21.2% at 24h.

It is interesting to note that the compressive strength correlates well with the CO₂ uptake (R² = 0.98612). The result suggests that the compressive strength is directly related to the CO₂ uptake. This is true that a higher CO₂ uptake contributes to the compressive strength due to the fact carbonation reaction increases the amount of CaCO₃ and C-S-H gel. However, it should be noted that carbonation reaction only contributes to the strength in the outer layer of the samples and the normal hydration contributes to the strength in the inner layer of the samples because the carbonation reaction only occurs in the outer layer of the samples.
Chapter 5

(a) Effect of CO$_2$ uptake on carbonation time

(b) Correlation between compressive strength and CO$_2$ uptake

Figure 5.8 Effect of carbonation time on CO$_2$ uptake of mortar and the correlation between CO$_2$ uptake and compressive strength
The phenolphthalein-stained cut surfaces of the mortar subjected to different carbonation times are shown in Figure 5.9. As expected, the 1h carbonation-cured sample had a relatively lower carbonation depth compared with the other times. However, carbonation depth showed relatively small change with a carbonation time of 2h or longer. This does not agree well with the rapid increase in CO₂ uptake over the same period, suggesting CO₂ cannot diffuse into the deeper layer of samples significantly, but instead, CO₂ interacts with the cement particles in the top layers.

Figure 5.9 Effects of carbonation time on carbonation profile
5.4.4 Effects of carbonation time on the microstructure of mortar

As can be seen from the phenolphthalein test, the top layer was highly carbonated after carbonation curing. The carbonated part was cut from the mortar samples in order to study the changes of morphology and reaction products due to different carbonation time. The cut carbonated samples were prepared for SEM and BSE analyses.

5.4.4.1 SEM images

The SEM images of fractured mortar samples both before the carbonation curing and after the carbonation curing at different carbonation times are presented in Figure 5.10. Two pieces of samples were collected for SEM tests for each formulation and for each piece of sample, around 15 micrographs were taken. The EDS analysis of five points is shown in Table 5.1. Figure 5.10(a) shows the mortar sample before the carbonation curing. It can be seen that it is mainly dominated by a loose structure, with predominantly clinker phases and C-S-H gel being clearly visible. Table 5.1 shows that the Ca/Si ratio of point 1 in Figure 5.10 (a) is about 3.2. Figure 5.10(b) shows the same mortar sample after being carbonation-cured for 1h. It is evident that some cubic CaCO$_3$ was formed, coexisting with some C-S-H gel, but CH was not observed. This suggests that CH could be the first phase to be carbonated. This is in agreement with the previous studies which suggest the dissolution rate of Ca$^{2+}$ from CH is higher than that from C-S-H gel (Trapote-Barreira et al., 2015, Haga et al., 2005). When the mortar sample was carbonated for 2h, the originally formed C-S-H gel was no longer observed, but instead, small crystals of CaCO$_3$ attached to the C-S-H gel were seen, as shown in Figure 5.10(c) and Figure 5.10 (d). In addition, the sample appears less porous when compared to the sample with only 1h carbonation. The sample became even more dense with the longer carbonation time of 4h (Figure 5.10 (e)). Small crystals of CaCO$_3$ are attached to the C-S-H gel. In addition, it seems that another type of CaCO$_3$ besides the cubic shape was formed, with a fibrous shape that is embedded in samples, as seen in Figure 5.10 (f). The mortar sample become further densified with the carbonation time of 24h (Figure 5.10 (g)). Figure 5.10 (h) is the magnification of
Both cubic and fibrous CaCO$_3$ were formed and can be clearly observed and intermixed with each other (Figure 5.10(h)). The cubic CaCO$_3$ is associated with calcite (Jiang et al., 2018) while the fibrous CaCO$_3$ is more likely to be associated with aragonite, another polymorph of CaCO$_3$ (Fermani et al., 2017, Tadier et al., 2017). After carbonation, irrespective of the analysis is taken (points 2 - 5), the Ca/Si ratio was always greater than the Ca/Si ratio of the parent cement. This is clearly indicative of intermixing of calcium carbonate and C-S-H.
Figure 5.10 SEM images of mortar subjected to different carbonation time

Table 5.1 EDS analysis of samples subjected to different carbonation time

<table>
<thead>
<tr>
<th>point</th>
<th>Sample</th>
<th>Ca</th>
<th>Si</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Fe</th>
<th>S</th>
<th>Ca/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Before carbonation</td>
<td>11.75</td>
<td>3.65</td>
<td>1.37</td>
<td>69.63</td>
<td>0.42</td>
<td>0.17</td>
<td>0.65</td>
<td>3.2</td>
</tr>
<tr>
<td>2</td>
<td>2h carbonation</td>
<td>10.05</td>
<td>2.29</td>
<td>27.39</td>
<td>56.96</td>
<td>0.79</td>
<td>0.22</td>
<td>0.33</td>
<td>4.39</td>
</tr>
<tr>
<td>3</td>
<td>4h carbonation</td>
<td>22.26</td>
<td>4.09</td>
<td>16.69</td>
<td>48.55</td>
<td>0.83</td>
<td>0</td>
<td>0.95</td>
<td>5.44</td>
</tr>
<tr>
<td>4</td>
<td>24h carbonation</td>
<td>40.23</td>
<td>5.68</td>
<td>10.47</td>
<td>42.32</td>
<td>0</td>
<td>0</td>
<td>0.76</td>
<td>7.08</td>
</tr>
<tr>
<td>5</td>
<td>24h carbonation</td>
<td>25.97</td>
<td>3.97</td>
<td>12.99</td>
<td>54.43</td>
<td>0</td>
<td>1.11</td>
<td>0.51</td>
<td>6.54</td>
</tr>
</tbody>
</table>
5.4.4.2 BSE images

Polished samples were prepared to illustrate the microstructural and phase changes with different carbonation times. The bright sections of the images are associated with clinker phases, the black sections with the pores, and the grey phases with C-S-H gel and calcium carbonates (Winter, 2012). The BSE images of the mortars subjected to microwave-based preconditioning and different carbonation times are presented in Figure 5.11. The EDS results related to the BSE images are presented in Table 5.2. The sample before carbonation in Figure 5.11(a) shows a high proportion of black areas which greatly reduce after 2h carbonation in Figure 5.11(b) with the proportion of grey sections increasing after carbonation. This indicates the original calcium silicates were converted into C-S-H gel and CaCO₃. This can be explained by the mechanism of carbonation curing. The $CO_2^-$ ions produced from the dissolved CO₂ and the $Ca^{2+}$ produced from the dissolved calcium silicates undergo rapid precipitation. This reaction reduces the $Ca^{2+}$ ions in solution and thus enables a rapid dissolution of calcium silicates, increasing the consumption of calcium silicates. The consumption of calcium silicates produces CaCO₃ and C-S-H gel, which increases the solid volume after carbonation curing. This is in agreement with the study by Tu et al. (2018) in which they have indicated that after carbonation, 1 mole of C₃S and C₂S could increase the molecular volume by 108.7% and 92.5%, respectively. Figure 5.11(c) presents a micrograph of the carbonated samples after 24h carbonation. This image also shows reduced amount of calcium silicates and more C-S-H gels, indicating further carbonation of calcium silicates has incurred.
In the previous study where a paste with high degree of hydration was analysed by BSE images (Lothenbach et al., 2007), a dark coloured ring was often observed surrounding the unreacted clinker, and this was considered as the inner C-S-H gel which has a higher Ca/Si ratio than the rest of the matrix. In Figure 5.11(a), there is a thin C-S-H gel layer surrounding the unreacted clinker before carbonation, probably due to the lower degree of hydration at that time. Interestingly, after carbonation curing, a thicker layer surrounding the unreacted clinker was observed in Figure 5.11(b) and (c), which is even thicker in the 24h carbonated sample. The Ca/Si ratio within this layer (points 2 and 4 in Table 5.2)
are much lower at 0.43 and 0.8, respectively, than the conventional C-S-H gel (approximately 1.7) (Matschei et al., 2007). This low Ca/Si ratio C-S-H gel layer can only be produced from the carbonation of calcium silicates and C-S-H gel. Because the C-S-H gel layer before carbonation (Figure 5.11 (a)) is thin, the thicker C-S-H gel must be partly produced from the carbonation of calcium silicates. This further demonstrates the accelerated consumption of calcium silicates via carbonation curing. The low Ca/Si ratio C-S-H gel may be explained by the fact that a C-S-H gel with an average Ca/Si ratio is initially formed at the beginning of carbonation, but as Ca is later removed from the gel as carbonation proceeds, the C-S-H gel thus has a lower Ca/Si ratio. This gradual loss of Ca from the C-S-H gel has also been observed by other researchers (Groves et al., 1991, Trapote-Barreira et al., 2015, Haga et al., 2005). The EDS results from points 1 and point 3 also showed a high Ca/Si ratio (5.4 and 7.2, respectively) after carbonation, indicating CaCO$_3$ could have been intermixed in the matrix which corroborates well the results in Section 5.4.4.1. It should be noted that the Ca/Si ratio in the images in Section 5.4.4.1 can be affected by topography difference, with the Ca/Si ratio for BSE images is more accurate. For both types of images, the Ca/Si ratios show a value consistent with intermixed CaCO$_3$ and C-S-H gel.

<table>
<thead>
<tr>
<th>point</th>
<th>Sample</th>
<th>Element/ Atomic %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>2h carbonation</td>
<td>Ca 15.99 Si 2.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 78.59 Al 0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe 0 S 0.76</td>
</tr>
<tr>
<td>2</td>
<td>2h carbonation</td>
<td>Ca 7.72 Si 18.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 72.49 Al 0.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe 0.25 S 0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ca/Si 0.43</td>
</tr>
<tr>
<td>3</td>
<td>24h carbonation</td>
<td>Ca 20 Si 1.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O 76.71 Al 0.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe 0.17 S 0.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ca/Si 7.2</td>
</tr>
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<td>24h carbonation</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>O 69.95 Al 0.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe 0.53 S 0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ca/Si 0.80</td>
</tr>
</tbody>
</table>

5.4.5 Effects of carbonation time on the reaction products of paste

As stated before, paste samples were prepared to investigate the reaction products in order to avoid any interference from aggregates. Immediately after the microwave-based preconditioning and carbonation curing, the top 0-2 mm
and the top 6-8 mm of the paste samples were drilled. These two layers were purposely selected to represent the layers of a higher degree and a lower degree of carbonation, respectively. The effects of carbonation time on the reaction products were then investigated with XRD and TGA.

(1) XRD

Figure 5.12 shows the XRD patterns of the top 0-2 mm layer of microwave-based preconditioned samples subjected to different carbonation times. Before carbonation (0h), peaks for calcite, calcium silicates and C₄AF were detected, which are the main components of Portland cement. Peaks for CH and ettringite were also detected arising from the hydration of calcium silicates and calcium aluminates. After carbonation for 1h, the intensity of the peaks for calcite increased and was accompanied by the disappearance of the peaks of CH and AFt, and a decrease in the intensity of the calcium silicates peaks. This indicates that calcium silicates are consumed during the carbonation curing which has led to the increased formation of CaCO₃. This has also been observed in other studies (Monkman and Shao, 2006, Mo et al., 2017, Tu et al., 2016, Zhang and Panesar, 2018b). At 2h, higher peak intensities of calcite are evident and a peak for aragonite emerges, with a further decrease in the main calcium silicate peaks. The newly formed aragonite possibly arises from the carbonation of the C-S-H gel. A further increase in the peaks for calcite was also observed at 4h and 24h, owing to the continued transport and reaction of CO₂ with the cement particles. Of all the carbonation products, the intensity of peaks for aragonite increased more significantly than any of the other peaks, from only a negligible peak at 1h to a small amount at 2h and then very noticeable peak at 24h. These results suggest that most of the crystalline CaCO₃ that formed after 2h carbonation is aragonite rather than calcite.
Figure 5.12 XRD patterns of the top 0-2 mm layer of microwave-based preconditioned samples subjected to different carbonation times

The XRD patterns for the top 6-8 mm layer of the microwave-preconditioned and carbonated samples at different carbonation times are shown in Figure 5.13. Compared with the sample before carbonation curing (0h), it is apparent that a longer curing time also leads to a lower content of calcium silicates and a higher amount of calcite. Peaks for ettringite and CH were also identified with higher peak intensities for CH at 1h compared with the 0h sample. With 2h carbonation and longer, the peak intensities of CH and AFt have both decreased, but they could still be detected between 2h and 24h. However, in all samples of the top 6-8 mm layer, the peak for aragonite was not observed. This correlates with the results from the 1h carbonation of the top 0-2 mm layer where no aragonite was detected at relatively low degrees of carbonation.
Figure 5.13 XRD patterns of the top 6-8 mm layer of microwave-based preconditioned samples subjected to different carbonation times

(2) TGA
Figure 5.14(a) shows the TG/DTG analysis curves of the top 0-2 mm layer of the samples subjected to different carbonation times. The peak for CH, with its characteristic DTG peak at ~ 450°C, was present in the 0h sample but not observed in other samples. This proves that all CH has been consumed during the carbonation curing process, which correlates with the XRD results where no CH was detected in the carbonated samples. CaCO$_3$ decomposes between 500°C and 1000°C in a series of characteristic peaks. The peaks for CaCO$_3$ increase with carbonation time, indicating carbonation continues with longer carbonation times leading to a higher degree of carbonation.

Three modes of the decomposition of calcium carbonate were proposed by Thiery (2007). Mode I was the decomposition of well-crystallised calcite, with the decomposition temperature between 780°C and 1000°C. Mode II was the decomposition of a less perfectly crystalline calcite and vaterite as well as aragonite, with a decomposition range of 680°C and 780°C. Mode III was the decomposition of amorphous CaCO$_3$, with a temperature range between 500°C
and 680°C. However, no obvious peaks above 780°C were observed in Figure 5.14, suggesting that the reaction products in the current project were different and it is uncertain whether using these fixed temperature intervals could be able to accurately represent the different carbonate phases of CaCO₃. The Zone I and Zone II in the DTG curve of the sample with carbonation for 2h are used as an example to show how the two zones are defined in Figure 5.14 (a). Clearly, the decomposition of CaCO₃ split into only 2 zones. Zone I represents decomposition temperatures between around 500°C and 640°C due to amorphous CaCO₃ and Zone II between around 640°C and 800°C to crystalline CaCO₃. Zone II is possibly a mixture of well-crystallised CaCO₃ and less perfectly crystalline CaCO₃, as seen from the sharp peaks with slight hump in the XRD peak for calcite. As from the DTG curve, the start and end point temperatures of the different “zones” are rather arbitrary, the precise temperature ranges were determined by second derivative curve (DDTG) in the current project (Kim and Olek, 2012).

Figure 5.14 (b) shows the DDTG curves of the samples taken from highly carbonated layer with different carbonation times. The decomposition temperature of Zone II of the 0h sample was between 640°C and 770°C. After carbonation, the start point temperature did not change for all samples, but the end point temperature shifted to higher temperatures, 800°C between 1h and 4h, and 817°C at 24h. The decomposition temperature range for Zone I was the same between 500°C and 640°C. Thus a higher degree of carbonation raised the decomposition temperature of Zone II although the decomposition temperature of zone I remained the same.
Figure 5.14 TG/DTG/DDTG analysis of microwave-based preconditioned samples subjected to different carbonation time (top 0-2mm)
Chapter 5

The TG/DTG curves of the top 6-8 mm layer of the samples subjected to different carbonation times are shown in Figure 5.15(a). Peaks for CH were evident in the 0h and 1h samples, but were insignificant with longer carbonation time. This correlates with the XRD patterns where the peaks for CH seen in the 2h, 4h and 24h carbonated samples were very weak. The peaks for the CaCO₃ increased steadily in intensity until at 24h, similar to those in the top 0-2 mm layer. The peak differences for CaCO₃ appeared to be larger in the first 4h of carbonation, but less between 4h and 24h samples. This is likely because the transport of CO₂ was higher at first, but then decreased due to the formation of a thick coating of CaCO₃ and denser microstructure.

Figure 5.15(b) gives the DDTG curve for samples from the top 6-8 mm layer with different carbonation times. The decomposition temperature range of Zone I for all samples was the same. The decomposition temperature range of Zone II for the 0h sample lay between 640°C and 770°C, with the end point temperature increasing to 780°C at 1h. Long carbonation times increased the end point temperature of Zone II to 808°C at 2h and 817°C at 24h. The difference in the decomposition temperature can be associated with different degrees of carbonation and accordingly, different degree of consumption of calcium silicates, as seen in the BSE images. This demonstrates that a higher degree of carbonation results in a more crystallised product leading to a higher end point temperature of Zone II.
Figure 5.15 TG/DTG/DDTG analysis of microwave-based preconditioned samples subjected to different carbonation time (top 6-8mm)
The amount of H$_2$O lost from the decomposition of C-S-H gel in the highly carbonated (top 0-2 mm) layer and semi-carbonated layer (top 6-8 mm) of the paste samples was calculated based on the weight loss between 105°C and 400°C (Shao et al., 2014), as shown in Figure 5.16. The amount of H$_2$O lost reflects the amount of C-S-H gel present. Compared with the sample before carbonation (0h), the amount of C-S-H gel increased steadily with carbonation time. This growth of C-S-H gel is one source of strength (CaCO$_3$ is the other source of strength) and its increase is one of the primary reasons for the strength development of samples after carbonation curing. This noticeably increased amount of C-S-H gel is possibly due to accelerated hydration of calcium silicates, which can be found from the BSE images (Figure 5.11).

It is interesting to note that the water loss due to C-S-H gel from the top 0-2 mm layer was generally lower than that from the top 6-8 mm layer, with the greatest difference being in the 24h carbonated sample. This may be because part of the C-S-H gel in the top 0-2 mm layer has been decomposed due to carbonation.

![Figure 5.16 Changes in the amount of H$_2$O decomposed from the C-S-H gel](image)

Figure 5.16 Changes in the amount of H$_2$O decomposed from the C-S-H gel
The CO$_2$ uptake for each carbonate phase of CaCO$_3$ in the two layers is calculated from the TG results based on the weight loss of CaCO$_3$. Changes in the amounts of different carbonate phases of CaCO$_3$ of the two layers are presented in Figure 5.17. The CO$_2$ uptake increased steadily with carbonation time for samples in both the top 0-2 mm layer and the top 6-8 mm layer. In the top 0-2 mm sample in Figure 5.17(a), the amount of CaCO$_3$ in Zone I remains stable after carbonation for 2h, but its percentage in the total CaCO$_3$ drops gradually. This is because crystalline CaCO$_3$ (Zone II) is continuously formed. These results agree with the XRD data where more aragonite was formed at the same time in Figure 5.12, generally giving rise to CaCO$_3$ in Zone II (Thiery et al., 2007). In contrast, in the top 6-8 mm layer, the amount of amorphous CaCO$_3$ increased between 1h and 4h and then remained stable up to 24h. This can be explained that amorphous CaCO$_3$ phase always forms first and then is converted to crystalline CaCO$_3$ over time as the crystalline CaCO$_3$ is a more thermodynamically stable phase (Ogino et al., 1987). When the rate of formation of amorphous CaCO$_3$ and the rate of conversion to crystalline CaCO$_3$ become the same, the amount of amorphous CaCO$_3$ remains the same. As a result, between 4h and 24h, the percentage of amorphous CaCO$_3$ remained unchanged but crystalline CaCO$_3$ continued to increase.
Figure 5.17 CO₂ uptake for different layers and percentages of different carbonate phases
5.4.6 Discussion

Microwave-based heating is a new preconditioning method, which can affect the threshold carbonation time. In this section, the effects of carbonation time are discussed in terms of three aspects, namely, 1) strength, CO$_2$ uptake and carbonation depth; 2) the carbonate phases of CaCO$_3$, and 3) the Ca/Si ratio of C-S-H gel.

(1) Effects of carbonation time on compressive strength and CO$_2$ uptake and carbonation depth

Increasing the carbonation time from 1h to 2h improved the compressive strength from 14 MPa to 27 MPa. The compressive strength continued to increase with carbonation after 2h, but at a much lower rate, reaching 33 MPa and 53 MPa at 4h and 24h. The CO$_2$ uptake increased continuously with the carbonation time, but interestingly, no significant change in the carbonation depth was observed after 2h. This is possibly because after 2h, while CO$_2$ can be absorbed in the top layer it does not readily diffuse further into the inside of the samples. This can be explained by the reduced permeability caused by the increase in volume of the carbonation of calcium silicates and CH. This could also be explained that the higher carbonation time increased partially carbonated region. Such zone cannot be tested by phenolphthalein test which changes colour at around 8.3.

As can be seen from the XRD analysis of the paste, calcium silicates were consumed in comparison to the reference (0h carbonation sample) to produce a low Ca/Si ratio C-S-H gel and CaCO$_3$, which are also reported in the previous studies (Monkman and Shao, 2006, Mo et al., 2017, Tu et al., 2016, Zhang and Panesar, 2018b). The reactions are described by Eq.5.1 and Eq.5.2. As this occurred, the porosity was greatly decreased, as can be seen from the BSE images. This is in agreement with previous studies which investigated the changes in the pore structures (Zhang and Shao, 2018, Lu et al., 2018, He et al., 2016, Neves Junior et al., 2015). The increased amount of C-S-H gel and
CaCO$_3$, and refined pore structure are the primary reasons that carbonation curing improves the compressive strength.

\[
C_3S + (3 - x)CO_2 + yH_2O \rightarrow xCaO\cdot SiO_2\cdot yH_2O + (3 - x)CaCO_3 \tag{5.1}
\]

\[
C_2S + (2 - x)CO_2 + yH_2O \rightarrow xCaO\cdot SiO_2\cdot yH_2O + (2 - x)CaCO_3 \tag{5.2}
\]

In the paste samples, the CO$_2$ uptake for the top 0-2 mm layer increased from 2.27% at 1h to 14.33% at 2h, but only increased to 18.42% at 24h. This shows the rate of CO$_2$ uptake slows down after 2h carbonation, which may be caused by development of a coating of CaCO$_3$ around the cement particles in the top layer due to carbonation reactions (Sharma, 2018; Seo, 2018; Guo, 2018). Therefore, while the strength in the highly carbonated layer can be increased with carbonation time, the rate of increase is slower after 2h.

As carbonation curing gives rise to higher strength, a greater carbonation depth of mortar leads to a higher compressive strength. The carbonation depth for the mortar samples increased significantly from 0h to 2h, but there was little increase from 2h to 24h, as seen from the phenolphthalein test. The compressive strength increases rapidly in the first 2h. While the extent of transport of CO$_2$ can increase with further carbonation time it is not significant to affect the carbonation depth of the mortar samples.

A deeper layer, though not measured in this study, is expected to be little affected by the carbonation reaction and will continue to hydrate as time proceeds without any influence from the carbonation reaction.

In summary, the carbonation reaction contributes to most of the strength in the first 2 hours by enhancing the strength of the outer layers of samples. After 2h carbonation, although the compressive strength continues to increase with time, it is mainly due to the ongoing hydration in the inner layer of the samples.

(2) Effects of carbonation time on the carbonate phases of CaCO$_3$
Both crystalline and amorphous CaCO$_3$ are produced during the carbonation curing process. As can be seen from the TG analysis, in the top 0-2 mm layer, the amount of amorphous CaCO$_3$ increases rapidly in the first 1h of carbonation, but does not change with further carbonation. Instead, crystalline CaCO$_3$ increases continuously with carbonation time up to 24h. In comparison, in the top 6-8 mm layer, while the amount of amorphous CaCO$_3$ increases in the first 4h, it then remains stable afterwards.

The changes in the ratios of the carbonate phases of CaCO$_3$ are very likely to be caused by the different carbonation rates of the hydration products, as has been observed in the normal carbonation process (Groves et al., 1991, Thiery et al., 2007). CH tends to react much earlier than C-S-H gel due to the higher dissolution rate of Ca$^{2+}$ from CH than from C-S-H gel (Trapote-Barreira et al., 2015, Haga et al., 2005). This is also observed in this project where the SEM images after 1h carbonation show the coexistence of the original C-S-H gel and CaCO$_3$ but the absence of CH and AFt, indicating CH and AFt are more susceptible to the carbonation reaction. During carbonation curing, the carbonation of CH tends to form crystalline CaCO$_3$ with higher thermal stability until most CH is removed, and then the C-S-H gel carbonates initially to produce CaCO$_3$ with lower stability (Thiery et al., 2007). In the top 6-8 mm layer, the amorphous CaCO$_3$ phase continues to increase from 0-4h due to the continual carbonation of C-S-H gel. However, when the partially carbonated C-S-H gel started to carbonate even further from 4h to 24h, it is more likely that amorphous CaCO$_3$ is formed first and converted to crystalline CaCO$_3$ rapidly, so that the content of amorphous CaCO$_3$ does not increase while its percentages decreases.

XRD results of the cement pastes show clearly that calcite is the predominant crystalline phase produced after carbonation. This phase (calcite) has been widely reported in previous studies where carbonation curing was applied (Monkman and Shao, 2006, Mo et al., 2017, Tu et al., 2016, Zhang and Panesar, 2018b). Aragonite was only observed in the highly carbonated layer of the paste samples with carbonation time over 2h. Changes in the amount of aragonite were noticeable with time, from nothing detected in the first 1h of
carbonation to a small amount after 2h carbonation and increasing to a noticeable amount after 24h carbonation.

As far as the author is aware, it is still unclear how the different carbonate phases of CaCO$_3$ are formed, but it seems that the aragonite is more likely to be formed when the C-S-H gel is the main carbonation target (Shtepenko et al., 2006, Black et al., 2007, Borges et al., 2010). For example, Shtepenko et al. (2006) found aragonite as the carbonation product of PC. In that study, PC paste was prepared with w/c ratio of 0.1 and then exposed to CO$_2$ pressure of 2 bar. After carbonation, the samples were ground and mixed with water again. The whole procedure was repeated 5 times. It was confirmed that the high degree of carbonation of the C-S-H gel produced aragonite. Black et al. (2007) also concluded that the carbonation of C-S-H with a low concentration of CO$_2$ for a long time always resulted in amorphous calcium carbonates first, but the carbonation of C-S-H gel with Ca/Si ratio < 0.5 produced aragonite predominantly and silica gel. They also proposed that the mechanism may be aragonite tends to form preferentially on the surface of the silica gel. Borges et al. (2010) found that aragonite was only present in the samples with low content of CH but high content of C-S-H gel during the normal carbonation process. In this project, the Ca/Si ratio of C-S-H gel becomes low as calcium is gradually removed from the C-S-H gel upon carbonation. After 2h carbonation, the Ca/Si ratio of C-S-H is so low that its carbonation produces aragonite. For example, the Ca/Si ratios surrounding the calcium silicates after 2h carbonation were low (<0.8) (from the BSE images in Figure 5.11), which probably proves the claim that carbonation of low Ca/Si ratio C-S-H gel produces aragonite.

In summary, calcite is the predominant carbonate phase of CaCO$_3$ in the carbonation curing process. The carbonation of PC also produces amorphous CaCO$_3$ initially, but further carbonation of PC produces aragonite with increased carbonation time.

(3) Effects of carbonation time on C-S-H gel
As can be seen from the SEM images, the C-S-H gel present after 1h of carbonation can be seen but the typical C-S-H gel morphology disappeared between 2h and 24h. This change has also been observed in a previous study where a C-S-H gel with a high Ca/Si ratio was converted to a low Ca/Si C-S-H gel, as observed by SANS (Thomas et al., 2004). In the current project, the change in morphology could also be likely to be due to a change in the stoichiometry of C-S-H gel, as shown in Eq. 5.3.

\[ C_xSH_y + CO_3^{2-} \rightarrow C_{x'}SH_{y'}, + CaCO_3 + H_2O; x > x' \quad 5.3 \]

At the first contact of the preconditioned samples with CO₂, CH and C-S-H gel were present and it was possible that the CH was consumed more rapidly than the C-S-H, as the dissolution of Ca²⁺ ions from CH is much higher than that from the C-S-H gel (Trapote-Barreira et al., 2015). The dissolution of C₃S was accelerated due to the presence of CO₃²⁻ by the formation of the precipitate (Maria Jose Sánchez-Herrero et al., 2017), CaCO₃, as seen in the Eqs. 6.1 and 6.2. These reactions produce CaCO₃ and C-S-H gel.

With the consumption of CH, ongoing reaction with CO₂ removes the interlayer Ca in the C-S-H. This removal of Ca then brings about excess negative charges, which are readily balanced through the formation of Si-OH groups (Chen et al., 2006). The neighbouring Si-OH groups then condense to form Si-O-Si links, which leads to polymerisation of the C-S-H gel that increases the mean chain length of C-S-H gel. This polymerisation of the C-S-H gel has been observed in PC samples after carbonation curing when observed by NMR (Shtepenko et al., 2006, Rostami et al., 2012a). In this case, the Ca²⁺ ions released from C-S-H leave the remaining C-S-H gel with a lower Ca/Si ratio (Trapote-Barreira et al., 2015, Berger et al., 1972, Shtepenko et al., 2006, Morandeau et al., 2014). In this study, a darker rim around the clinker phases was clearly observed in the BSE images. EDS analysis of these rims does indeed show a low Ca/Si ratio (<1), indicating Ca has been gradually released from the C-S-H into the matrix to precipitate as CaCO₃.
However, the lower Ca/Si ratio of the C-S-H gel in the matrix was not detected via SEM-EDS in the current study which showed a much higher Ca/Si ratio (4 ~ 7) after carbonation than the conventional Ca/Si ratio (around 1.7). This agrees with the previous studies where a high Ca/Si ratio has also been observed after carbonation curing (Ashraf, 2016, Jia and Richardson, 2018, Escalante-Garcia et al., 1999, Richardson, 1999). This is likely because the leaching of Ca from the C-S-H gel results in an immediate precipitation of CaCO$_3$ which is intimately intermixed with the remaining C-S-H gel so it is difficult to identify the pure C-S-H gel in the SEM and SEM-BSE images.

In summary, carbonation of the C-S-H gel often results in a change in silicate polymerization and a lower Ca/Si ratio (< 1) C-S-H gel. The silicate polymerization may increase and Ca/Si ratio reduce with carbonation time. In most cases, the remaining C-S-H gel is intermixed with CaCO$_3$ tightly.
5.5 Effects of CO$_2$ pressure on the mortar subjected to microwave-based preconditioning

5.5.1 Introduction

As discussed in Section 2.5.6, the CO$_2$ pressure determines its dissolution in pore solution and also its transport through the cement paste. The concentrations of CO$_3^{2-}$ and H$^+$ in the pore solution affects the rate of carbonation reaction and possibly the carbonation products. In addition, the rate of CO$_2$ transport is a primary factor that influences the carbonation reaction.

Microwave heating is a new preconditioning method with a different heating mechanism when compared to the current preconditioning methods (Zhang et al., 2017, Pan et al., 2017, Rostami et al., 2011). Due to its volumetric heating nature, the microwave-based preconditioning takes much less time than the current existing preconditioning methods (70 min vs. 6-18h). Whilst the fast preconditioning duration could be an advantage by reducing the whole curing time, the porosity is expected to be higher and the degree of hydration of samples could be lower under microwave heating due to the short preconditioning time, which, in turn, could influence the rate of CO$_2$ transport. To address these issues, in this section, the influences of CO$_2$ pressure on the strength, carbonation efficiency and the microstructure of the mortar and carbonation products of the cement paste were investigated in an attempt to identify any potential contribution that higher CO$_2$ pressure could make to resolve these issues.

5.5.2 Effects of CO$_2$ pressure on the properties of mortar

5.5.2.1 Effects of CO$_2$ pressure on the compressive strength of mortar

After microwave-based preconditioning for 70 min, mortar samples (w/c ratio of 0.37) were subjected to hydration or carbonation for 2 hours at different CO$_2$ pressures. The samples being microwave preconditioned and then hydrated for 2h is denoted as the reference sample. The effects of CO$_2$ pressure on the compressive strengths of mortar are shown in Figure 5.18. It can be seen that
the reference sample exhibited the lowest strength, with only 6.7 MPa recorded. The samples exposed to 0.5 bar and 1 bar CO$_2$ pressure showed higher strengths, reaching 15.3 MPa and 27.2 MPa, respectively. However, strength increases at higher pressures were not significant, with similar strengths obtained at 3 bar and 5 bar. A similar trend was observed by Ahmad et al. (2017) and Shi and Wu (2008), who found the threshold pressures of 1.2 bar and 0.9 bar, respectively.

5.5.2.2 Effects of CO$_2$ pressure on CO$_2$ uptake and carbonation profile

The effects of CO$_2$ pressure on CO$_2$ uptake of the mortar samples following microwave-based preconditioning and 2h carbonation are shown in Figure 5.19. The samples exhibited a continual increase in CO$_2$ uptake with increasing CO$_2$ pressures from 0.5 bar to 5 bar, from 8.37% at 0.5 bar to 9.29% at 1bar. It then reached 10.9% at 5 bar. This steady increase in CO$_2$ uptake between 1 and 5 bar is, however, not in agreement with the strength development where little difference was shown.

![Figure 5.18 Effect of the CO$_2$ pressure on the strength of mortar after carbonation](image_url)
The phenolphthalein spray test was performed with the results being shown in Figure 5.20. Whilst minor differences in the carbonation profile were observed among the carbonated samples at pressures above 1 bar, the carbonation depth was the lowest in the sample subjected to 0.5 bar pressure. This trend correlates well with the strength results where 1 bar was also confirmed to be the threshold pressure for strength development.
The effects of CO₂ pressure on the microstructure of mortar were assessed from SEM and BSE images. Only the carbonated layers of the mortar were sampled for the microstructure analysis.

5.5.3.1 SEM images

The influence of the CO₂ pressure on the microstructure in the top layer of mortar is shown in Figure 5.21. Significant changes can be observed between...
the samples before and after carbonation curing, where C-S-H gel and CH were consumed in the carbonation reaction producing intermixed C-S-H gel and CaCO$_3$. Little difference was observed in samples subjected to between 0.5 bar and 5 bar pressures.

Figure 5.21 Mortar subjected to different CO$_2$ pressures
5.5.3.2 BSE images

Figure 5.22 shows the BSE images of the polished mortar samples subjected to different CO$_2$ pressures before and after carbonation. A significant increase in the volume of reaction products was observed after carbonation curing, although the difference between pressures of 1 bar and 5 bar was small.

(a) before carbonation  
(b) 1bar-1  
(c) 5bar

Figure 5.22 BSE images of mortar subjected to different CO$_2$ pressures
EDS was also performed to examine the Ca/Si ratio in the matrix in Table 5.3. The Ca/Si ratios in the matrix are very similar at the different carbonation pressures, with a value recorded around 5.4 which is much higher than the conventional C-S-H gel (approximately 1.7) (Matschei et al., 2007). This again shows an intimate intermix of CaCO$_3$ and C-S-H is present in the matrix of both mortar samples.

Table 5.3 EDS analysis of BSE samples subjected to different CO$_2$ pressures

<table>
<thead>
<tr>
<th>point</th>
<th>Ca</th>
<th>Si</th>
<th>O</th>
<th>Al</th>
<th>Fe</th>
<th>S</th>
<th>Ca/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.69</td>
<td>3.53</td>
<td>74.22</td>
<td>0.53</td>
<td>0.18</td>
<td>1.08</td>
<td>5.57</td>
</tr>
<tr>
<td>2</td>
<td>15.99</td>
<td>2.96</td>
<td>78.59</td>
<td>0.65</td>
<td>0</td>
<td>0.76</td>
<td>5.4</td>
</tr>
</tbody>
</table>
5.5.4 Effects of CO₂ pressure on carbonation products in cement paste

Paste samples were prepared in order to avoid any interference of sand. The effects of CO₂ pressure on the reaction products were again investigated with XRD and TGA. In this section, BC refers to paste samples before carbonation but after preconditioning.

(1) XRD
Figure 5.23 (a) shows the highly carbonated layer (top 0-2 mm) of the cement paste subjected to different pressures. As already shown in Section 5.4, calcium silicates, CH and AFt are significantly consumed in the carbonation process. Generally, the carbonated products in samples subjected to different carbonation pressures were similar, with calcite being the predominant crystalline carbonation product. In addition, no peaks for AFt and CH were detected in all the carbonated samples, indicating that they had been completely consumed. Weak peaks for aragonite were identified only in the 3 bar and 5 bar cured samples, with the latter producing slightly more aragonite. Based on Henry’s law, a higher pressure would increase the concentration of carbonic ions in the pore water, however, the changes in concentration do not produce significantly different reaction products.

Figure 5.23 (b) shows the top 6-8 mm layer of the cement paste subjected to different pressures. High intensity peaks for calcite were also observed but no aragonite was detected. This correlates with the conclusion in Section 5.4 and further demonstrates that a higher degree of carbonation facilitates the formation of aragonite. Peaks for both CH and AFt were initially present in the top 6-8 mm layers of the paste samples, but these decreased with higher pressures. The increased carbonation with higher pressures suggests that the pressure can increase the rate of transport of CO₂ into the top 6-8 mm layer.
Figure 5.23 XRD patterns of the samples subjected to different CO$_2$ pressures
(2) TG results

Figure 5.24(a) shows the TG/DTG analysis of highly carbonated layer (top 0-2 mm) in the paste samples subjected to different CO\textsubscript{2} pressures. It can be seen that the characteristic DTG peak for CH was reduced after carbonation, whilst the intensities of the peaks for CaCO\textsubscript{3} was enhanced, indicating the consumption of CH and the formation of CaCO\textsubscript{3}. Generally, for the top 0-2 mm layers for the samples subjected to different pressures, the differences are insignificant. This corroborates with the XRD patterns that the different pressures do not produce significantly different reaction products though they result in different concentrations of dissolved CO\textsubscript{2} based on Henry’s law.

Figure 5.24 (b) shows the TG/DTG analysis of the semi-carbonated layers in the paste samples subjected to different carbonation pressures. Compared to the top 0-2 mm layer, more differences for CaCO\textsubscript{3} were seen in the top 6-8 mm layers.
Figure 5.24 TG/DTG analysis of microwave-based preconditioned samples subjected to different CO$_2$ pressures
Figure 5.25 shows the level of CO₂ uptake for the top 0-2 mm and top 6-8 mm layers of cement pastes. The differences between the samples in the top 0-2 mm layer are relatively small, with the total CO₂ uptake increasing slightly from 13.49% at 0.5 bar to 14.35% at 5 bar. In contrast, the CO₂ uptake for the top 6-8 mm layer increases significantly from 8.25% at 0.5 bar to 13.18% at 5 bar. Comparing these results with the CO₂ uptake for the top 0-2 mm layer, it can be concluded that the top 6-8 mm layer is more influenced by CO₂ transport than the top 0-2 mm layer which is directly exposed to CO₂.

![Graph showing CO₂ uptake for cement pastes](image)

Figure 5.25 CO₂ uptake for the highly carbonated (top 0-2 mm) and semi-carbonated (top 6-8 mm) layer of cement pastes subjected different CO₂ pressures
5.5.5 Discussion

The effect of CO\textsubscript{2} pressure on the degree of carbonation can be attributed to its increased dissolution in the pore solution and its influence on the rate of the transport. The increased dissolution may affect the reaction mechanism, and the rate of the transport may affect the carbonation depth.

(1) Effect of CO\textsubscript{2} pressure on reaction mechanism

The dissolution of CO\textsubscript{2} in water can be described by Henry’s law (Eq. 6.4) (Carroll et al., 1991). Based on Henry’s law, it is clear that a higher CO\textsubscript{2} pressure gives rise to a higher concentration of CO\textsubscript{2} in the pore water and as a consequence, the concentrations of \(CO_3^{2-}\) and \(H^+\) increase in the pore solution. The reaction mechanism may also be different due to the difference in the concentrations of the reactants.

\[
C = \frac{K_p}{K_h}
\]

where \(K_p\) is the partial pressure of the gas, \(K_h\) is the Henry’s constant and \(C\) is the concentration of dissolved CO\textsubscript{2} in pore water.

In normal carbonation where a low CO\textsubscript{2} partial pressure is applied (below 1 bar), there is no real consensus in the published data on the influence CO\textsubscript{2} pressures have on carbonation products. Castellote et al. (2009) showed that carbonation of cement with a CO\textsubscript{2} concentration of 3\%, seemed to change the microstructure of the C-S-H gel giving a higher degree of polymerization. In contrast, Visser (2014) proposed that the differences in the carbonation products were due to incomplete carbonation, and different concentrations of CO\textsubscript{2} would eventually result in the same carbonation products provided sufficient reaction time could be given.

The results of this study are consistent with the opinion of Visser (2014) where similar carbonation products are found after carbonation at different pressures.
between 0.5 bar and 5 bar. Firstly, in the top 0-2 mm layer of the paste samples subjected to different pressures, the XRD results show similar carbonation products and the TG results show a similar CO₂ uptake. Secondly, in the carbonated layers of the mortar samples, the samples subjected to different pressures show similar SEM images (intermixed C-S-H gel and CaCO₃) and the Ca/Si ratio of C-S-H gel in the BSE images is similar with an intermixed CaCO₃ and C-S-H gel. These results demonstrate the limited influence of CO₂ pressure between 0.5 bar and 5 bar has on the reaction products. The concentrations of \( CO_3^{2-} \) and \( H^+ \) may be higher with higher partial pressure of CO₂, which increases the reaction speed. However, after 2h carbonation, they finally achieve similar final carbonation products.

(2) Effect on the rate of CO₂ transport

The rate of transport of CO₂ is one of the most important parameters in carbonation. The gaseous CO₂ can dissolve in the pore water first and then diffuses into the samples through solution, and the gaseous CO₂ can also diffuse into the samples first through air and then dissolve in the pore water locally. This is further elaborated as follows: (1) According to Henry’s law, the concentrations of \( CO_3^{2-} \) and \( H^+ \) ions in the pore water increase as pressure increases. Then with a higher pressure, the concentrations of \( CO_3^{2-} \) and \( H^+ \) are higher and thus can diffuse into the samples at a higher rate due to a larger concentration gradient; (2) The number of CO₂ gas molecules also increase with the pressure (according to ideal gas law), and diffuse into the samples via concentration gradient; (3) the CO₂ gas molecules diffuse into the samples via pressure gradient (Phung et al., 2015, Zou et al., 2015), and thus the rate of transport also increases with pressure. In summary, higher CO₂ pressure increases both the transport of dissolved CO₂ and the gaseous CO₂ into the samples.

In the current study, the effects of CO₂ pressure on the strength of microwave-based preconditioned mortars show that there is a threshold pressure (1 bar),
above which there is little increase in strength of mortar when further pressure increases. Similar trends were also observed in the phenolphthalein test.

A threshold pressure has also been observed in the previous studies reported in the literature. Young et al. (1974) cast their C₃S mortar by compaction and then placed the sample in the CO₂ chamber at different pressures (1 bar, 2 bar and 4 bar) for 3 min. Their results showed 2 bar was their threshold pressure. However, Shi and Wu (2008) preconditioned lightweight aggregate concrete in a dry environment (RH of 55%) for 4h then exposed the samples to different CO₂ pressures (0.7 bar, 1.4 bar and 2.1 bar) for 2h and found only small differences among the three CO₂ pressures. Furthermore, Ahmad et al. (2017) preconditioned concrete specimens for 18h in a sealed mould before placing them in the CO₂ chamber at different pressures (from 0.7 bar to 4.2 bar). Generally, they also found the effect of CO₂ pressure on strength was insignificant.

In the current study, the mortar samples were preconditioned by microwave heating for 70 min before being put into the CO₂ chamber. Compared with the previous studies, the porosity of the samples was expected to be high due to the relatively short microwave-based preconditioning time. However, the threshold pressure is not significantly different when compared with those reported in the literatures.

In the paste samples, both XRD and TG analysis show that the CO₂ uptake in the top 6-8mm layer of the paste sample significantly increases with CO₂ pressure but the value in the top 0-2 mm layer only increased slightly, suggesting that the higher pressures lead to an increased transport rate of CO₂, driven by the concentration and pressure gradient. This can also explain that increasing the pressure from 0.5 bar to 1 bar increased the carbonation depth of the mortar sample.

However, the observed higher transport in the paste does not lead to a noticeably deeper carbonation depth in the mortar with pressures over 1 bar, as seen in the phenolphthalein test. As discussed in Section 5.4, the porosity was
greatly decreased after carbonation, as can be seen from the BSE images, which is expected to reduce the permeability in the top layer of the mortar samples. This is in agreement with previous studies which showed a refined pore structures after carbonation curing (Zhang and Shao, 2018, Lu et al., 2018, He et al., 2016, Neves Junior et al., 2015). The higher pressures increase the rate of transport of CO$_2$. However, the permeability in the top layer of the mortar will be reduced significantly due to the expansive carbonation reaction which is an important factor that influences the rate of transport of CO$_2$. As a consequence, a higher pressure could not necessarily lead to deeper penetration of CO$_2$ into the samples. In this study, 1 bar pressure could be considered as the threshold pressure for the microwave-based preconditioning and carbonation regime.

In summary, CO$_2$ pressure influences the rate of transport of CO$_2$, but it is not great enough to affect the carbonation depth when the pressure exceeds 1 bar. There is no indication that pressure has any effect on the carbonation reaction itself.
5.6 Conclusion

It can be seen from the discussions above that microwave-based heating can provide an efficient preconditioning method prior to carbonation curing in a considerably shorter time than the conventional preconditioning procedures. A marked improvement in compressive strength can be achieved after 70 minutes of microwave heating followed by 2h carbonation with significant CO\textsubscript{2} uptake.

The effects of three factors, namely, preconditioning time, carbonation time and CO\textsubscript{2} pressure on the properties and degree of carbonation of the cementitious samples were studied. The main conclusions can be summarized as follows.

(1) Effects of preconditioning time

- Increasing the microwave-based preconditioning time up to the threshold time leads to a much higher degree of carbonation and related compressive strength. Further increasing the preconditioning time beyond the optimum shows little increase in carbonation efficiency or strength development. The optimum preconditioning time varies with w/c ratio being 70 min for samples with a w/c ratio of 0.37 and 90 min for samples with a w/c ratio of 0.5.
  - The threshold preconditioning time is very close to the final setting time.
  - The microwave-based heating proves to be a time-efficient preconditioning method due to its volumetric heating nature.

(2) Effects of carbonation time

- The carbonation depth of mortar increased significantly with carbonation time from 1h to 2h but exhibited little change when the carbonation time was further increased up to 24h. The increase in strength between 2h and 24h could be primarily attributed to the ongoing hydration in the uncarbonated layer. The threshold carbonation time is determined as 2h.
  - The percentages of crystalline CaCO\textsubscript{3} and amorphous CaCO\textsubscript{3} change with carbonation time and are likely to be attributed to the different reaction rates of CH and C-S-H gel with CO\textsubscript{2}.
Calcite is the predominant polymorph of crystalline CaCO$_3$, with aragonite only produced at high degrees of carbonation.

The Ca/Si ratio of C-S-H gel in the matrix is expected to be reduced after carbonation, however, the Ca/Si ratio detected in the matrix is higher than that in the conventional C-S-H gel. This could be mainly attributed to the intermixed C-S-H gel and CaCO$_3$ produced.

(3) Effects of CO$_2$ pressure

- There is significant improvement in compressive strength and carbonation depth of mortar when the CO$_2$ pressure increases from 0.5 bar to 1 bar. However, little further improvement was observed when the pressure was increased from 1 bar to 5 bar, although there was a small but steady increase in the CO$_2$ uptake. Thus, 1 bar pressure could be considered as the threshold pressure.
- Increasing the CO$_2$ pressure from 0.5 bar to 5 bar does not significantly change the carbonation products in the highly carbonated layer (top 0-2 mm) of the paste sample.
Chapter 6  Comparison of microwave heating with other methods for preconditioning cementitious materials

6.1 Introduction

As discussed in Chapter 5, microwave-based preconditioning (MP) has shown positive effects on the degree of carbonation and gives greatly improved compressive strength after carbonation curing. In this chapter, to identify the efficiency of microwave-based preconditioning, MP is compared with other preconditioning methods reported in the literature in terms of their effects on the carbonation efficiency, microstructure and reaction products of cement paste and mortar before and after carbonation curing.

6.2 Experimental programme

6.2.1 Introduction

In Chapter 2, it was concluded that in order to apply the carbonation curing to concrete, in particular, the concrete with sufficient workability which can be cast by vibration, an additional process known as preconditioning, is needed to remove water after the concrete is cast prior to carbonation curing. The dominant preconditioning methods currently reported in the literature include exposure to lower humidity (described as air preconditioning in this thesis) and steam curing (Zhang and Shao, 2018, Shi et al., 2012a, Rostami et al., 2011).

In this chapter, the microwave-based preconditioning method is compared with water bath heating (WP) - a simulation to the steam curing but with more accurate control to the temperature history, air preconditioning (AP) and no-preconditioning (NP) in terms of their effects on the properties, microstructure, and reaction products of cementitious materials before and after carbonation curing.
WP was selected in this study to represent steam curing. The reason is that they both are subjected to a RH close to 100% during the heating process, but the rate of internal temperature rise in the WP sample can be adjusted to that close to the MP sample, while the steam cured sample cannot reach such a high rate of temperature rise.

AP was selected as it is a conventionally used method in the literature to remove water before carbonation curing. In this study, the amounts of water evaporated in the AP sample and in the MP sample were controlled to be similar.

NP was also included in this study. However, it should be highlighted that this is different from other methods because the w/c ratio in the NP sample was 0.15, which is suitable for subsequent carbonation curing without any preconditioning but only can be moulded by compaction.

6.2.2 Experimental programme

For the preconditioned samples (MP, WP and AP), a w/c ratio of 0.37 was used for the mortar and paste and the samples were moulded by vibration to simulate the procedure followed by precast industry. For the sample without preconditioning (NP), a w/c ratio of 0.15 was used for the mortar and paste. Before they were placed in the carbonation chamber, the NP mortar sample was mixed and compacted, while the NP paste sample was mixed and dispersed as powder on a plate.

The experimental programme was conducted in the following 2 stages.

**Stage 1:** the mortar and paste samples subjected to different preconditioning methods but before going through carbonation curing were studied by measuring the water distribution, microstructure and hydration products. The temperature and RH history were also monitored to better understand the state of samples during the preconditioning process. The microstructure was
examined by SEM and BSE, and the hydration products were characterized with XRD and TG.

Stage 2: the mortar and paste samples subjected to different preconditioning methods and after going through carbonation curing were studied in terms of the compressive strength, carbonation efficiency, microstructure and hydration products. The carbonation efficiency was assessed by CO$_2$ uptake and phenolphthalein spray test. The microstructure was examined by SEM and BSE, while the hydration products were characterized with XRD and TG.

Experimental details of the related preconditioning methods are listed in Table 6.1 below.

<table>
<thead>
<tr>
<th>Preconditioning methods</th>
<th>w/c ratio</th>
<th>Way of moulding</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>0.37</td>
<td>Vibration</td>
<td>Microwave heating for 70 minutes</td>
</tr>
<tr>
<td>WP</td>
<td>0.37</td>
<td>Vibration</td>
<td>Water bath heating for 70 minutes</td>
</tr>
<tr>
<td>AP</td>
<td>0.37</td>
<td>Vibration</td>
<td>In-mould preconditioning under 50% R.H. and 20 ± 1 °C for 5 hours, and then cured under the same condition after stripping the moulds for another 19 hours</td>
</tr>
<tr>
<td>NP</td>
<td>0.15</td>
<td>Compaction (mortar); Dispersed powder (paste)</td>
<td>No preconditioning</td>
</tr>
</tbody>
</table>
6.3 Effects of preconditioning methods on the properties of mortar and paste prior to carbonation curing

6.3.1 Introduction

To better understand the conditions and status of the mortar samples prior to carbonation curing, the temperature and RH history inside the samples and in the surrounding environment were monitored, respectively. It should be noted that the NP sample was exposed to carbonation curing directly without any preconditioning.

6.3.2 Temperature and relative humidity (RH) history during the preconditioning process

6.3.2.1 Temperature inside the mortar samples

The real-time temperature changes at different depths inside the samples were measured by inserting a 3-grating optical fibre sensor into the sample, with their locations being given in Section 4.4.1.1. It should be noted that with MP the internal temperature of the sample is closely controlled by adjusting the microwave power, while for the WP and AP samples, the temperature of the surrounding environment is controlled (as this is the case when these two techniques are used in practice). Figure 6.1 and Figure 6.2 show the temperature evolution of the MP and WP mortar samples. The MP sample showed a small temperature gradient between the three layers during the first 15 minutes, whilst the temperature gradient of the WP sample was relatively large in the first 15 minutes, although negligible in the subsequent preconditioning process. For the AP sample, as it was placed in the 20°C environment for 24 hours, changes of the temperature inside the samples can be ignored due to the small size of the samples even though cement hydration may release a small amount of heat.

The different temperature gradients in the first 15 minutes between MP and WP samples are caused by their different heating mechanisms. For the MP, the heating mechanism is volumetric heating (Shi, 2017, A.K.Datta, 2001). This
refers to the microwave energy being converted into heat in the sample instantly and homogeneously, resulting in a small temperature gradient from surface to core of the samples. For the WP sample, heating is transferred by conduction from the environment to the samples, thus causing a larger temperature gradient.

The top surface of MP sample showed a relatively lower temperature than the deeper layers after 15 minutes. This is because the MP sample was heated from inside and the surface of the sample was exposed to air directly (almost ambient temperature) which results in cooling. In contrast, the WP sample was heated from outside to inside.
Figure 6.1 Temperature evolution during the MP process

Figure 6.2 Temperature evolution during the WP process
6.3.2.2 Temperature and RH in the surrounding environment of the mortar samples

Figure 6.3 shows the temperature of the environment surrounding the samples subjected to the three preconditioning methods. As it can be seen, there was a steady increase in the temperature for the MP sample, rising from 20°C to 30°C in the first 20 minutes and then remaining constant afterwards, while the temperatures for the WP and AP samples were maintained constant. The RH of the environment for each preconditioning method was also monitored and shown in Figure 6.4. The RH for the MP samples was stable at 50% for the first 20 minutes but decreased to around 37% at 70 minutes during the heating process. For the AP sample, the RH was maintained at 50%. However, the RH for the WP sample was expected to be around 100% because the sample was carefully sealed. It should be noted that for the MP and WP, the duration of heating was only 70 minutes, but for AP the sample was exposed to room temperature for 24h.
Figure 6.3 Temperatures of the surrounding environment related to different preconditioning methods

Figure 6.4 Relative humidity (RH) of the environment related to different preconditioning methods
6.3.3 Water distribution of mortar samples

As stated earlier in Chapter 4, water added into the mortar during mixing was converted into four types of water, namely, evaporated water 1 (water lost during preconditioning), evaporated water 2 (water lost after preconditioning but prior to carbonation), combined water and remaining free water.

Figure 6.5 shows the distribution of water inside the mortar samples after being subjected to different preconditioning methods. It can be seen that the percentage of remaining free water was the highest in the WP sample (77.6%), followed by the MP (61.5%) and AP samples (54.5%). The difference of the remaining free water content between the MP and WP samples was mainly attributed to the loss of the evaporated water 1, where as much as 20.1% of the water was lost from the MP sample but none was lost in the WP sample; this rapid water evaporation from the MP sample during preconditioning can be seen as an unique advantage of microwave heating. The difference of the remaining free water content between the MP and AP samples was mainly attributed to the combined water, with the values of 7.8% and 14.4% recorded, respectively, though the total water evaporated during and after heating were similar for MP and AP (30.7% and 31.1%, respectively). But AP took 24h to achieve this while WP only took 70 min. It should be noted that the role of combined water is unique because combined water could not affect the transport of CO₂ at the beginning of the carbonation process, but it can be released during carbonation curing.
(a) MP

(b) WP
Figure 6.5 Water distributions of samples exposed to different preconditioning methods

(c) AP
6.3.4 Microstructure of the mortar before carbonation

(1) SEM images

The NP sample is not included in this section because the samples are largely unhydrated clinker phases. Figure 6.6 presents the fractured surface of the mortar samples after being subjected to the three different preconditioning methods. Clinker phases are noticeable in the MP and WP samples, which is due to their relatively low degree of hydration. In contrast, more hydration phases are visible in the AP sample with large crystals of CH present. These images show that the degrees of hydration under the different preconditioning regimes are different, with the AP sample showing the highest degree of hydration which has been achieved from the long preconditioning time and, hence, more time to hydrate.
Figure 6.6 SEM images of mortar samples subjected to different preconditioning methods
(2) BSE images

It should be noted that the NP sample was collected immediately after compaction, and thus little hydration is to be expected. In the BSE images, the bright sections of the images are clinker phases, the black portions are pores, and the grey phases are C-S-H gel, AFt and CaSO₄ (Winter, 2012). The clinker phases were identified as ‘C’ for C₃S, C₂S, C₃A and C₄AF, ‘S’ for CaSO₄. Figure 6.7 shows the BSE images of the mortar samples subjected to different preconditioning methods. The images of the MP and WP samples show a higher amount of clinker phases and lower amount of hydration products in comparison to the AP sample. This correlates with the SEM images above and the phase analyses in Section 6.3.5. The NP sample shows little hydration with only few hydration products observed (Figure 6.7(d)). This again indicates the different degrees of hydration for the different preconditioning methods, with the AP has the highest degree of hydration and the NP has the lowest degree of hydration.

With the different degrees of hydration (as seen from the amounts of combined water in Figure 6.5), porosity appears different in the BSE images. The porosities of the MP, WP are significantly higher than the AP sample which has a higher degree of hydration. The higher porosity of MP and WP may thus enable a higher rate of transport of CO₂ in the subsequent carbonation curing. This can be seen in the previous studies where a higher porosity generally gave rise to the CO₂ transport in the cementitious materials (Houst and Wittmann, 1994, Shi et al., 2016b). In addition, the porosity of the NP sample appears to be lower in comparison to the MP and WP samples despite being the lowest degree of hydration. This may be due to its much lower w/c ratio and the different way of moulding where compaction rather than the vibration was used.
6.3.5 Characterization of cement paste before carbonation

Cement pastes instead of mortar samples were prepared to avoid the influence of sand in the phase analysis in the current study. The samples were subjected to a similar preconditioning regime to the mortar samples and then characterized with XRD and TG. Again the NP sample was not included below as it was considered to have undergone only little hydration at this stage.

Figure 6.8 shows the XRD patterns of the cement pastes after being subjected to the different preconditioning methods. Peaks for CH and ettringite were
identified in all the samples. Relatively stronger peaks for CH and ettringite and weaker peaks for calcium silicates were observed in the AP sample compared to the MP and WP samples, indicating more hydration had occurred in the AP sample. In addition, the peaks for CH and ettringite for the MP sample is slightly higher than that in the WP sample, suggesting a slightly higher degree of hydration. In all the three samples, peaks for calcite were present, which is considered to be from limestone contained in the cement.

![XRD patterns of cement paste subjected to different preconditioning methods](image)

Figure 6.8 XRD patterns of cement paste subjected to different preconditioning methods

The TG/DTG data of cement pastes subjected to different preconditioning methods is depicted in Figure 6.9. The peaks for CH and C-S-H gel, with the characteristic DTG peak at ~ 450°C and ~130°C, are present in all the samples. The intensities of the CH and C-S-H gel peaks for the MP and WP samples are much lower than those in the AP sample. This correlates with the XRD analysis and previous SEM images where the AP sample demonstrates the highest degree of hydration. The intensities for CaCO₃ is also higher for the AP sample, which may be due to the carbonation of CH when preparing for the samples, as there were no particular measures to avoid natural carbonation.
The weight loss of combined water between 105°C and 500°C, related to the degree of hydration, is also calculated in the figure. It was found that the combined water for the MP sample (2.32%) was higher than that for the WP sample (1.84%). The temperature history was controlled to be the same for the MP and WP samples. The difference between the amounts of combined water can be because the temperature gradient within the specimens, thus making the sampling less representative. It is also possible that the non-thermal effect induced by microwave heating occurred, which refers to the higher degree of hydration in microwave heating than conventional heating with same temperature history.

![Figure 6.9 TG/DTG of cement paste subjected to different preconditioning methods](image)

The microwave non-thermal effect could be due to the reduction of activation energy of the hydration reaction, which is the energy required to initiate the reactions (Shibata et al., 1996, Wroe and Rowley, 1996, Janney et al., 2005, Wang et al., 2006, Lin et al., 2009, Nomanbhay and Ong, 2017). The reduction can be attributed to the mechanism of microwave heating that rotates the dipoles, and thus increasing the probability of the colliding of molecules and
atoms. This phenomenon has been found in numerical studies (Shibata et al., 1996, Wroe and Rowley, 1996, Janney et al., 2005, Wang et al., 2006, Lin et al., 2009, Nomanbhay and Ong, 2017). Shibata et al. (1996) compared the effect of conventional heating and microwave heating on the disintegration reaction of NaHCO₃, and it was found that the activation energy was reduced by the microwave radiation. Fukushima et al. (2013) studied the reduction reaction of CuO with microwave heating and conventional heating. The microwave energy can be separated into an electrical field and magnetic field, and it was found that the activation energy reduced by 2/3 in the electrical field (117 kJ/mol) and by 1/3 in the magnetic field (228 kJ/mol) compared to that in conventional heating (292 kJ/mol). In this study, the non-thermal effect of microwave heating on the degree of hydration still needs further study, as the confirmation of the effect requires more data and precise experiments.

In summary, the AP sample had a higher amount of combined water, indicating a much higher degree of hydration and longer preconditioning time than the MP and WP samples, which led to a lower porosity.
6.4 Effects of preconditioning methods on properties of mortar and cement paste after carbonation

After being subjected to the different preconditioning methods, the mortar and cement paste samples were carbonated for 2h at a CO_2 pressure of 5 bar. The effects of the preconditioning methods on samples after carbonation were compared in terms of compressive strength, carbonation efficiency, microstructure and carbonation products.

6.4.1 Effects of different preconditioning methods on the compressive strength of mortar

The compressive strengths of mortars before and after carbonation are given in Figure 6.10. In general, significantly higher strengths were observed in the mortar samples after carbonation. For the MP sample, the compressive strength was 1.6±0.23 MPa before carbonation, but increased by 26 MPa to 27.59±1.3 MPa after carbonation. Compared with the MP sample, the WP sample had a lower strength after carbonation, with 21.12±0.62 MPa recorded. This suggests that with a similar temperature profile as well as the same preconditioning and carbonation time, MP as a preconditioning method gave a noticeably higher strength after carbonation curing. The reason can be explained when considering WP sample lost a lower amount of water. Other researchers have shown that a lower amount of water loss in the preconditioning process resulted in a higher amount of remaining water that impeded CO_2 transport and reduced the degree of carbonation curing (Shi et al., 2012a, Morshed and Shao, 2014). For the NP samples, the strength was barely measurable before carbonation, but they developed the highest strength after carbonation. It should be noted that the NP samples were cast by compaction rather than vibration, and the sample size was smaller than the other groups, so care should be taken when comparing it with other groups.

For the AP sample, the compressive strength before carbonation was 15.03±1.24 MPa, but became 30.98±2.69 MPa after carbonation curing, suggesting carbonation curing contributes 16 MPa to the samples. AP is a
conventional method for preconditioning concrete, but it did not develop much higher strength than the MP sample after carbonation curing and took a much longer time to reach it (24h vs. 70 min). The MP sample shows a higher compressive strength increase (26 MPa) than the AP sample (16 MPa). This demonstrates the high preconditioning efficiency of microwave heating for the subsequent carbonation curing. The reasons can be explained as follows.

As can be seen in Eqs. 6.1, 6.2 and 6.3, the total carbonation of C₃S, C₂S and CH can increase the solid volume by 108.7, 92.5 and 11.5%, respectively (Tu et al., 2018, Shi et al., 2016a). The carbonation of C₃S and C₂S reduces the porosity significantly and forms a low Ca/Si ratio C-S-H gel. The carbonation of CH also reduces the porosity, but not as significant as C₃S and C₂S. Thus, the carbonation of C₃S and C₂S, which reduces strength and produces C-S-H gel, contributes a higher strength than the carbonation of CH. The AP sample has a higher degree of hydration with less C₃S, C₂S and more CH present in comparison to the MP and WP sample. As a consequence, the increase rates for the MP and WP samples are higher than that for the AP sample.

\[
\begin{align*}
C_3S + CO_2 + H_2O & \rightarrow CaO\cdot SiO_2 \cdot H_2O + CaCO_3 \\
C_2S + CO_2 + H_2O & \rightarrow CaO\cdot SiO_2 \cdot H_2O + CaCO_3 \\
CH + CO_2 + H_2O & \rightarrow CaCO_3
\end{align*}
\]

In summary, with a similar preconditioning time (70 min) as well as temperature profile and carbonation regime, the MP sample developed 30% higher strength than the WP sample after carbonation. With similar amounts of evaporated water, a relatively higher strength was obtained in the carbonated AP sample than the MP sample, but the MP process shows a much a higher increase in compressive strength and saves 95% time needed for the AP process.
6.4.2 Effects of different preconditioning methods on the carbonation efficiency

The carbonation efficiency is assessed with CO$_2$ uptake and carbonation depth. The CO$_2$ uptake of samples subjected to different preconditioning methods after carbonation curing is shown in Figure 6.11. A higher CO$_2$ uptake was observed in the MP sample than the WP sample, with values of 10.9% and 7.9%, respectively. The AP sample showed a comparable CO$_2$ uptake with the MP sample, with the value of 11.2% recorded. The NP sample has not been recorded because it was of different size and moulded by compaction.
In the phenolphthalein spray test, the colourless part shows the depth to which the samples are highly carbonated. The carbonation depths of samples subjected to the three preconditioning methods after carbonation are shown in Figure 6.12. All samples showed a similar carbonation pattern: a higher depth of carbonation in the top layer and lower in the bottom layer. This carbonation shape may be caused by the fact that more water was lost from the top layer and the least from the bottom layer in the evaporation process because water can only evaporate from the top layer.

The WP sample showed a lower carbonation depth than the MP sample, which is consistent with the results of the compressive strength and CO₂ uptake. This can be explained by the lower amount of water evaporated from the WP sample. As water can only be lost from the surface of samples, the WP sample may have an excess amount of water in the deeper layer, thus impeding the rate of CO₂ transport which is related to the degree of carbonation curing (Shi et al., 2012a, Morshed and Shao, 2014). It is interesting to note that the carbonation
depth for the AP sample is lower than the MP sample, which will be explained in Section 6.5.

Figure 6.12 Effects of preconditioning methods on carbonation profile (a) MP; (b) WP; (c) AP

6.4.3 Effects of different preconditioning methods on the microstructure of mortar after carbonation

It has been mentioned above that the different preconditioning methods led to different degrees of hydration prior to carbonation, which could possibly lead to the differences in microstructure after carbonation. The phenolphthalein test showed that only the top layers were highly carbonated for all samples. In this section, the fractured surfaces of the carbonated products in the top layers were compared. Polished samples were also prepared for BSE images.

6.4.3.1 SEM images

Figure 6.13 shows the changes in the morphology of the MP samples after carbonation. The morphology differs from the samples before carbonation that the AFt and CH crystals are not observed. More importantly, there were needle-like materials present before carbonation, but those materials disappeared after carbonation curing, which are expected to be the intermixed C-S-H gel and CaCO$_3$. Small crystals, which are likely to be CaCO$_3$, are attached to the surface of matrix containing both CaCO$_3$ and C-S-H gel (Figure 6.13 (b)).
The morphology of the WP sample after carbonation is also different to that before carbonation (Figure 6.13(c) and (d)). The unhydrated phases have disappeared and are replaced with a more polymerized gel, with small CaCO$_3$ crystals attached to the matrix containing both CaCO$_3$ and C-S-H gel.

The morphology of the AP sample after carbonation is shown in Figure 6.13(e) and (f). The AP sample also showed an intermixed CaCO$_3$ and C-S-H gel. In addition, with a larger magnification, as seen in the top right corner of Figure 6.13 (f), clusters of CaCO$_3$ crystals were observed in the AP sample. This phenomenon was not present in other samples. It may arise from the carbonation of large crystals of CH, as seen in the SEM image of the AP sample prior to carbonation (Figure 6.6).

When the degree of hydration is low (such as the MP and WP samples), only small amounts of CH and C-S-H gel exist, and the most prominent phases remaining are calcium silicates. The dissolved Ca$^{2+}$ ions in the solution rapidly react with CO$_3^{2-}$ to form CaCO$_3$. The C-S-H gel may still form when calcium silicates are exposed to CO$_2$, due to its very low solubility (Juillard et al., 2010, Walker et al., 2016), and its formation was observed in the previous study (Berger et al., 1972). The CaCO$_3$ is intermixed with C-S-H because the precipitation of CaCO$_3$ and formation of C-S-H gel are both very fast. With a higher degree of hydration (such as in the preconditioned AP), the intermixed CaCO$_3$ and C-S-H gel are also observed. However, CH may form as large crystals discrete from C-S-H. CH is much more soluble than CaCO$_3$ and will only precipitate when the concentrations of Ca$^{2+}$ and OH$^-$ are high enough. Before carbonation, the Ca$^{2+}$ ions can readily move into the solution. This often results in a large crystal forming when CH eventually precipitates and separates from the C-S-H gel. But with carbonation, nano-CaCO$_3$ is formed in the position where the large CH was because of the rapid precipitation reaction, and thus results in an inhomogeneous distribution of CaCO$_3$ and C-S-H gel.
Figure 6.13 SEM images of mortar samples subjected to different preconditioning methods and carbonation curing
6.4.3.2 BSE images

The BSE images of the polished mortar samples subjected to carbonation curing after the different preconditioning methods are presented in Figure 6.14, and average Ca/Si ratio of over 30 points tested by EDS are shown in Table 6.2. These figures clearly show a more compact structure compared to the samples before carbonation shown in Figure 6.7. The BSE images again demonstrate that the volume of carbonation products is much higher than their parent phases, which is in agreement with the previous literatures showing that the carbonation of clinker phases and CH increased the solid volume (Tu et al., 2018, Shi et al., 2016a, Zhang et al., 2017, Rostami et al., 2012a). The reduction of clinker phases and the disappearance of CH were both observed in the BSE images after carbonation. The space between the clinker phases, originally filled with the pores, had narrowed and was connected by the newly created C-S-H gel. The significantly reduced porosity and the newly produced C-S-H and CaCO$_3$ are the reason for the strength development after carbonation (Zhang and Shao, 2018, Lu et al., 2018, He et al., 2016, Neves Junior et al., 2015).

The average Ca/Si ratio of all four preconditioned samples measured by EDS ranged from 5.11 to 5.18, suggesting relatively similar compositions in all four matrices, this showing that the four preconditioning methods gave similar chemical compositions in the hardened matrix comprising C-S-H gel and intermixed CaCO$_3$. The highly intermixed C-S-H gel with CaCO$_3$ is in agreement with the previous studies (Tu et al., 2018, Sharma and Goyal, 2018, Tu et al., 2016).
Figure 6.14 BSE images of samples subjected to different preconditioning methods after carbonation curing

Table 6.2 Average Ca/Si ratio of the matrix in mortar subjected to different preconditioning methods

<table>
<thead>
<tr>
<th></th>
<th>MP</th>
<th>WP</th>
<th>AP</th>
<th>NP</th>
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<tbody>
<tr>
<td>Ca/Si ratio</td>
<td>5.11</td>
<td>5.17</td>
<td>5.18</td>
<td>5.18</td>
</tr>
</tbody>
</table>
6.4.4 Effects of different preconditioning methods on the carbonation products of cement paste

As the different preconditioning methods give rise to different degrees of hydration, thus resulting in different proportions of C-S-H gel, CH and calcium silicates in the samples before carbonation. This may further influence the constitutions and proportions of the carbonation products.

Paste samples were prepared for subsequent phase analysis in order to avoid the interaction of aggregates. The reaction products were investigated with XRD and TGA. It should be noted that the NP sample was cement powder mixed with water (w/c ratio of 0.15) and then dispersed and exposed to CO$_2$ directly, so all samples collected were highly carbonated.

6.4.4.1 Characterisation of the highly carbonated layer of cement paste

(1) XRD

Figure 6.15 shows the XRD patterns of the highly carbonated layer (top 0-2mm) in samples subjected to different preconditioning methods. The samples subjected to MP, WP and AP show similar patterns: calcite is the predominant carbonation product with aragonite also present. This shows that the samples with different degrees of hydration give similar crystalline phases after carbonation curing. The NP sample showed a similar trend where lower peaks for C$_3$S and C$_2$S and higher peaks for calcite were observed. The presence of gypsum and anhydrite in all the samples may come from the carbonation of AFt, with the products formed after carbonation are gypsum and aluminate gel. In addition, the NP sample showed much higher peaks for gypsum and anhydrite than other samples, signalling they were not consumed in the carbonation reaction. This can be explained that gypsum and anhydrite cannot dissolve completely in the NP sample due to their relatively low solubility (0.207g/100g and 0.275g/100g at 25°C, respectively) (Bock, 1961) and the low water content (w/c ratio of 0.15).
Figure 6.15 XRD patterns of the highly carbonated layer (top 0-2 mm) of the samples subjected to different preconditioning methods after carbonation.

(2) TG

Figure 6.16 shows the TG/DTG/DDTG analysis of highly carbonated samples subjected to different preconditioning methods after carbonation. As mentioned in Chapter 5, the carbonation peaks are divided into Zone I and II, with the former considered to be the decomposition of amorphous CaCO$_3$ and the latter to be the decomposition of crystalline CaCO$_3$. The start point temperature and end point temperature of each zone were determined from the second derivative curve (Figure 6.16(b)). The temperature range for each carbonate phase of CaCO$_3$ is similar for each preconditioning method. In all four samples, the mass losses of C-S-H gel, with characteristic DTG peak at ~150°C, were also very similar, suggesting a similar amount of C-S-H gel is produced with the four different preconditioning methods.
Figure 6.16 TG/DTG/DDTG analysis of the highly carbonated layer (top 0-2mm) of samples subjected to different preconditioning methods after carbonation
The total CO$_2$ uptake and the percentages of each carbonate phase of CaCO$_3$ are presented in Figure 6.17. In the highly carbonated layer, the total CO$_2$ uptake was in the order of MP > WP > AP, with the range between 12.9% ~ 14.4% for the preconditioned samples. The percentages of amorphous CaCO$_3$ (zone I) to the total CaCO$_3$ produced were in the range of 29.6% ~ 31.2% in the preconditioned samples. The amorphous CaCO$_3$ phase is always formed first, and then converted to crystalline CaCO$_3$ phases (Ogino, 1987). This suggests that a high degree of carbonation gives similar total CO$_2$ uptake and relative percentages of amorphous CaCO$_3$ for the preconditioned samples despite there being differences in the degree of hydration prior to carbonation. The NP sample had a lower CO$_2$ uptake (11.2%) in comparison to the three preconditioned samples. This can be explained by the uncarbonated gypsum and anhydrite in the NP sample, as seen from the XRD patterns. In contrast, the gypsum and anhydrite almost disappeared in the MP, NP and AP samples, which probably contributed to the CO$_2$ uptake.

Figure 6.17 CO$_2$ uptake and the percentage of different carbonate phases of CaCO$_3$ in the highly carbonated layer (0-2 mm)
The four preconditioning methods all produce different degrees of hydration before carbonation, but appear to result in similar carbonation products. Without hydration, C_3S and C_2S are the main components for carbonation, while with high degree of hydration, the C-S-H gel and CH are the main components for carbonation (Marchon and Flatt, 2016, Bullard et al., 2011). Thus, two paths of carbonation are proposed (Figure 6.18). In path 1, the C_3S and C_2S are considered to dissolve in the water to produce dissolved Ca^{2+} and C-S-H gel in the solution. The CO_3^{2-} reacts with Ca^{2+} to form CaCO_3 and extract Ca from C-S-H gel. In path 2, it is the dissolution of CH, AFt and C-S-H in water to form CaCO_3 and C-S-H gel. Because the reactions in the two paths occur in solution (different degrees of hydration), the dissolved ions are of the same type and result in the same carbonation products. As a low degree of hydration generally requires a short preconditioning time, this shows that the carbonation reaction can start as early as possible to reduce the total preconditioning and carbonation curing duration.

Figure 6.18 Two paths for the carbonation of cement particles (adapted from Monkmana et al., 2018)
6.4.4.2 Characterisation of the semi-carbonated cement paste

(1) XRD

Figure 6.19 shows the XRD patterns of the semi-carbonated layer (top 6-8 mm) in the preconditioned samples. When comparing MP with WP, the MP sample had much lower peaks for C_3S, C_2S and CH while much higher peaks for calcite. This clearly indicates the WP sample had a lower degree of carbonation in the semi-carbonated layer when compared with the MP sample.

![XRD patterns](image)

Figure 6.19 XRD patterns of the semi-carbonated layer (top 6-8 mm) of the samples subjected to different preconditioning methods after carbonation.
Figure 6.20 shows the TG/DTG analysis of the semi-carbonated layer in the samples subjected to different preconditioning methods. The figure shows that the WP sample had a much lower degree of carbonation compared with the MP and AP samples, which agrees with the XRD results. Examining the peaks of CH and C-S-H gel, it is interesting to note that an increase in the peak for CH (AP > WP > MP) is related to an increase in the peak for C-S-H gel (AP > WP > MP). This can be explained that the carbonation of C-S-H starts after the carbonation of CH. Without the total, or at least local consumption of CH, C-S-H gel will not be carbonated (Groves et al., 1991, Thiery et al., 2007). It can also be seen that the decomposition temperatures are different. This can be due to the fact that amorphous CaCO$_3$ phase is formed first, and then converted to crystalline CaCO$_3$ phases (Ogino, 1987). As the MP sample has the highest degree of carbonation, more amorphous CaCO$_3$ in the sample is converted to crystalline CaCO$_3$ phase and leads to the highest decomposition temperature. In contrast, the WP sample has the least degree of carbonation, and the lowest decomposition temperature.
In the semi-carbonated layer, the WP sample shows a much lower total CO$_2$ uptake, calculated from the TG results (Figure 6.21). This clearly indicates that in the WP sample the semi-carbonated layer had a lower degree of carbonation compared to the MP and AP samples. This can be probably explained that in the WP sample the relatively high content of remaining water impedes the rate of transport of CO$_2$ and reduces the degree of carbonation.

Figure 6.21 CO$_2$ uptake for the semi-carbonated layer (top 6-8mm)
6.5 Comparison of microwave-based preconditioning (MP) with air-based preconditioning (AP) of samples before and after carbonation

6.5.1 Introduction

From the discussions above, the MP sample with its similar preconditioning time and temperature history, exhibited 30% higher strength than the WP sample, with 38% higher CO$_2$ uptake. A similar CO$_2$ uptake was observed in the highly carbonated layer (top 0-2 mm) of the MP and WP samples but a much lower value was recorded in the semi-carbonated layer (top 6-8 mm), suggesting that in the WP sample, it was difficult for CO$_2$ to penetrate deep to the inside. Therefore, WP was not subjected to further investigation. NP was also not compared because it was a different sample size and moulded in a different way.

With a similar amount of total evaporated water lost during the preconditioning process, the MP sample has a lower degree of hydration and higher porosity when compared to the AP sample, but they appear to show similar carbonation products and CO$_2$ uptake after carbonation. To better understand the effects of MP and AP on the carbonation of samples, the temperature rise of mortar samples in the carbonation process was monitored in this section. In addition, the characterization of carbonated layer and semi-carbonated layer in the cement paste subjected to each preconditioning method is presented in a different way to better understand the differences between the MP and AP preconditioning.

6.5.2 Temperature of mortar in the carbonation process

The temperatures reached by the MP and AP mortar samples during the carbonation process were monitored, as shown in Figure 6.22. They both showed a sharp initial rise in temperature peaking at 62.3°C at 5.2 min for the MP sample and 61.1°C at 7 min for the AP sample followed by a slow decrease. These temperature changes suggest the carbonation reactions in the first few
minutes are rapid, then the subsequent reactions slow down. In addition, the peak temperature of the AP sample was slightly lower than the MP sample, and showed a slight delay to reach the peak. This delay may be attributed to the fact that the AP mortar before carbonation is less permeable, as seen in the BSE images in Figure 6.7.

![Image](image.png)

**Figure 6.22** Temperatures of the MP and AP samples during the carbonation process

### 6.5.3 Characterization of the cement paste subjected to MP and AP

For each preconditioning method (MP and AP), three cement paste samples, namely, uncarbonated, highly carbonated and semi-carbonated samples are compared in this section. The uncarbonated sample refers to the sample immediately after preconditioning, while the highly carbonated and semi-carbonated samples were powders collected from the top 0-2mm and top 6-8 mm layers after preconditioning and 2h carbonation. In the text, shorthand notations are used to refer to the paste samples with MP and AP e.g. M70 stands for microwave-based preconditioning for 70 min, M70-C2h-top 0-2 mm
for the powder from the highly carbonated layer after 70 min microwave heating and 2h carbonation, A24h stands for air preconditioning for 24h.

Figure 6.23 shows the XRD patterns of the uncarbonated, highly carbonated (0-2 mm) and semi-carbonated (6-8 mm) samples conditioned by MP and AP. In the MP sample (Figure 6.23(a)), the peaks for the C₃S and C₂S were greatly reduced in the highly carbonated layer and semi-carbonated layer compared to the uncarbonated sample.

The AP sample also shows the consumption of C₃S and C₂S after carbonation curing (Figure 6.23(b)). It should be noted that in the semi-carbonated layer the peaks for C₃S and C₂S are much weaker in comparison to the highly carbonated layer, which is different again from that in the MP sample. As water can only evaporate from the surface of the sample, water content in the surface layer is supposed to be lower than the inside. The higher consumption of C₃S and C₂S in the deeper layer suggests that the top layer has been over-dried. This may be another reason for the lowered carbonation depth in the AP sample, besides a lower permeability in the AP sample, as described in Section 6.4.2. The over-dried surface in the AP sample was not observed in the MP sample, may be due to a more homogeneous water loss from the MP sample.

This more homogeneous water loss from the MP sample is likely to be due to an easier migration of moisture from the inside to the surface. Firstly, water can only evaporate from the top surface of the samples. When the top surface of the sample becomes semi-dry, the moisture gradient enables the moisture to migrate from the inside to the surface (Mujumdar, 2006). The microwave mechanism of heating is volumetric heating, which is different from conventional heating. This unique volumetric heating speeds up the migration of moisture inside samples compared with the conventional heating (Zhang et al., 2006). In addition, the volumetric heating may generate ‘vapour’ inside the sample which has a higher internal pressure so can move to the surface of samples quickly (Metaxas and Meredith, 1993, Song et al., 2016, Ni et al., 1999, Fu et al., 2017). In cementitious materials, entrapped air bubbles are formed in the mixing stage, and the unique volumetric heating is expected to expand the air bubbles as well,
and thus accelerates the water migration. This may thus promote a more homogeneous water distribution. Secondly, though the MP and AP samples have a similar water loss, the MP sample has a porous structure after only 70 min preconditioning in comparison to the AP sample after 24h hydration, as seen in the BSE images. These porous structures facilitate the migration of water from the interior to the surface (Roca et al., 2006, Roca et al., 2008, Yang et al., 2017, Baik and Marcotte, 2003). In a study, Roca et al. (2006) studied different porosities within a cereal composite food, and found that a higher porosity led to a higher water migration. Yang et al. (2017) investigated the moisture transport in fried potato chips with different porosities, and found that when porosities were high, the migration of water was quick due to the capillary action and vapour transport in the capillary pores. Baik and Marcotte (2003) studied the moisture diffusivity when baking cakes, and also found that the water migration is faster with higher porosities. With a noticeably higher porosity in the MP sample, the water transport is considered to be faster and may result in a more homogenous water distribution.
Figure 6.23 XRD patterns of the MP and AP samples before and after carbonation
6.6 Conclusion

This chapter has discussed the advantages and disadvantages of microwave-based preconditioning compared to other preconditioning methods. The conclusions drawn are as follows.

- A 30% higher compressive strength and 38% higher CO$_2$ uptake, and higher carbonation depth were observed for the MP mortar sample than that for the WP mortar sample. This is likely due to the much higher amount of water loss from the MP preconditioning process that facilitates the transport of CO$_2$, giving higher carbonation efficiency.

- With similar water losses from the AP and MP mortar samples, the MP process saves 95% preconditioning time of the AP process. In addition, a lower carbonation depth was found in the AP mortar sample. This is likely due to the lower porosity of the AP sample and over-drying of the top surface.

- The carbonation products were similar for all samples, irrespective of the differences in preconditioning methods. In addition, the CO$_2$ uptake and percentages of the different carbonate phases of CaCO$_3$ were similar in the highly carbonated layer of the preconditioned samples after carbonation.

- Clusters of CaCO$_3$ were found in the AP sample (high degree of hydration) after carbonation, whereas for the MP, WP and NP samples (low degree of hydration) a more homogeneous distribution of CaCO$_3$ was observed after carbonation.
Chapter 7  Effects of microwave-based preconditioning on the properties of carbonated PC blends

7.1 Introduction

As described in Chapters 5 and 6, microwave-based preconditioning is used in order to achieve efficient carbonation, which can significantly increase the early strength of mortar samples and sequester CO\(_2\) as well. It is well known that the replacement of cement with mineral additions in cementitious materials can reduce the carbon footprint; however, it can decrease the early strength (Moon et al., 2017, Thongsanitgarn et al., 2014, Soutsos et al., 2017). The low early strength can be potentially solved by applying the newly developed regime in Chapter 5. Thus, this chapter is aimed at extending the application of the newly developed established microwave-based preconditioning and carbonation regime to cement paste and mortar containing conventional mineral additions.

In this chapter, mortar and paste samples of PC blended with these three mineral additions, namely, fly ash, GGBS and limestone powder, were cured according to the microwave-based preconditioning and carbonation regime developed in Chapter 5. The effects they have on the preconditioning time were studied by assessing the strength development, CO\(_2\) uptake and carbonation depth after subsequent 2h carbonation curing. Then, mortar and paste samples with the appropriate preconditioning times were selected to investigate the influence of mineral additions on the microstructure, carbonation depth and carbonation products after carbonation curing. In addition, the evolution of compressive strength, microstructure and reaction products at 4h, 1d and 28d were also studied on the paste and mortar samples.

7.2 Aim and objectives

The aim of this study is to apply the microwave-based preconditioning and carbonation regime developed to mortar and cement paste with selected
mineral additions. Understanding the mechanism and performance will lay the foundation for its potential application in precast industry. To achieve this aim, three objectives are proposed.

(1) To obtain the threshold microwave-based preconditioning times for the PC blends containing fly ash, GGBS and limestone powder by assessing the strength development, CO₂ uptake and carbonation depth after subsequent carbonation curing.

(2) To study the influence of the mineral additions using the developed preconditioning times and carbonation regime on the carbonation depth, microstructure and carbonation products of PC blends.

(3) To investigate the evolution of compressive strength, microstructure, and reaction products of the PC blends from objective 2 at different ages.
7.3 Effects of mineral additions on the microwave-based preconditioning time suitable for subsequent carbonation curing

7.3.1 Introduction

In Chapter 5 the threshold microwave-based preconditioning time for carbonation curing was 70 min for a mortar prepared with pure cement. It is also suggested in Chapter 5 that this threshold time is close to its final setting time. Mineral additions in mortar can affect the setting time and microstructure, thus influencing the efficiency of microwave-based preconditioning so the threshold preconditioning time for mortar with pure cement may not be suitable for the mortar samples with additions. Thus, the suitability of preconditioning times for the mortar samples incorporating three most common mineral additions was assessed based on the compressive strength and carbonation efficiency of mortar. Before that, the three mineral additions are briefly introduced as below.

7.3.1.1 Fly ash

Fly ash is a waste material from the coal power plant with spherical particles. It contains both crystalline and amorphous phases. The crystalline phases are almost inert, while the amorphous phases are reactive and can react with alkalis to form a C-S-H gel. Based on BS 197-1:2011 (BSI, 2011), there are two types of fly ash, siliceous and calcareous. In this project, siliceous fly ash is used.

Siliceous fly ash cannot harden itself without the addition of alkalis. The glassy structure of the siliceous fly ash decomposes in the presence of CH produced from the hydration of cement (Qian et al., 2001). The dissolved silica and alumina in the alkaline environment form C-S-H gel, which can fill the pores and contribute to strength.

However, the pozollanic reaction of fly ash and alkalis proceeds slowly, resulting in low early strength. In the long run, the pozollanic reaction is noticeable and produces C-S-H gel, contributing to the long-term strength (Lam
et al., 2000, Sakai et al., 2005). Low early strength is the biggest problem for blending large amounts of fly ash with PC. Even when high-volume fly ash concrete is steam cured, the addition of fly ash still unavoidably results in a lower early strength (Yazıcı et al., 2005).

The study by Zhang et al. (Zhang et al., 2016) showed that carbonation cured concrete containing 20% and 40% fly ash after air preconditioning for 11.5h, exhibited higher early strength than their uncarbonated counterparts, demonstrating the potential of using carbonation curing to enhance the early strength of fly ash concrete.

7.3.1.2 GGBS

GGBS is a by-product from the process of manufacturing iron, which mainly contains glassy contents. Generally, ordinary GGBS hydrates slowly, but presents noticeable cementing properties when suitable activators are added (Neville, 2011). The hydration of GGBS is relatively slow in comparison with that of cement, which explains why the replacement of cement with GGBS can reduce the hydration heat (Wang et al., 2016). The setting time is delayed with the addition of GGBS (Beushausen et al., 2012). It is generally considered that the addition of GGBS reduced the compressive strength of cementitious materials, especially at early stage (Barnett et al., 2006).

Compared with pure PC, the GGBS is more sensitive to temperature (Barnett et al., 2006). The replacement of cement with GGBS in mortar cured at the ambient temperature greatly decreased early strength in comparison to the pure PC mortar, but the replacement did not show lower 3d strength than pure PC mortar at a curing temperature of 50°C (Barnett et al., 2006). However, in this study, the carbonation curing started with limited preconditioning time (70 ~ 90 min), it is expected that little hydraulic reaction of GGBS should occur before carbonation.
7.3.1.3 Limestone powder

Limestone powder is a by-product from the aggregate-crushing industry mainly in the form of calcite polymorph of calcium carbonate. The effects of limestone powder on the properties of cementitious materials are two-fold. On the one hand, the presence of fine limestone powder increases the rate of hydration of cement, thus increasing the early strength by forming nucleation sites for the precipitation of hydration products such as CH and C-S-H (Aqel and Panesar, 2016, Moon et al., 2017, Bentz et al., 2017, Thongsanitgarn et al., 2014). This can change the setting time of the mortar samples. The limestone powder can also fill the capillary pores and densify the structure (Bentz et al., 2017), which can reduce the permeability of the sample. On the other hand, the addition of limestone powder dilutes cement and thus it is expected to increase the permeability of cementitious materials.

The study by Tu et al. (2016) demonstrated a higher CO₂ uptake with the addition of limestone powder in cement, suggesting limestone powder may also serve as the nucleation sites for the carbonation reactions and increase the rate of carbonation reaction.

7.3.2 Experimental details

Table 7.1 illustrates the typical experimental details. The samples containing mineral additions were subjected to different preconditioning times and carbonation curing (5 bar CO₂ pressure) for 2h. The percentages of all the three additions were 35%, which is the upper limit for Cem II, as described in BS EN 197-1-2011 (BSI, 2011). The water/binder (binder refers to cement and mineral additions) ratio (0.37) was the same as that in the previous study, and the sand/binder ratio was 2. In this section, 'MP' stands for ‘pure cement without additions’, ‘FA’ stands for ‘fly ash’, ‘GS’ stands for ‘GGBS’, and ‘LS’ stands for ‘limestone powder’. Then GS90minC2, for example, stands for the curing regime for a mortar with 35% GGBS subjected to microwave-based preconditioning for 90 min and carbonation at 5 bar pressure for 2h.
Table 7.1 Typical experimental details

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Composition</th>
<th>Regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP70min</td>
<td>100% cement</td>
<td>Microwave heating for 70 min</td>
</tr>
<tr>
<td>MP70minC2</td>
<td></td>
<td>Microwave heating for 70 min and carbonation for 2h</td>
</tr>
<tr>
<td>FA70min</td>
<td></td>
<td>Microwave heating for 70 min</td>
</tr>
<tr>
<td>FA70minC2</td>
<td></td>
<td>Microwave heating for 70 min and carbonation for 2h</td>
</tr>
<tr>
<td>FA90min</td>
<td>35% fly ash + 65% cement</td>
<td>Microwave heating for 90 min</td>
</tr>
<tr>
<td>FA90minC2</td>
<td></td>
<td>Microwave heating for 90 min and carbonation for 2h</td>
</tr>
<tr>
<td>FA110min</td>
<td></td>
<td>Microwave heating for 110 min</td>
</tr>
<tr>
<td>FA110minC2</td>
<td></td>
<td>Microwave heating for 110 min and carbonation for 2h</td>
</tr>
<tr>
<td>GS70min</td>
<td></td>
<td>Microwave heating for 70 min</td>
</tr>
<tr>
<td>GS70minC2</td>
<td></td>
<td>Microwave heating for 70 min and carbonation for 2h</td>
</tr>
<tr>
<td>GS90min</td>
<td>35% GGBS + 65% cement</td>
<td>Microwave heating for 90 min</td>
</tr>
<tr>
<td>GS90minC2</td>
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<tr>
<td>GS110min</td>
<td></td>
<td>Microwave heating for 110 min</td>
</tr>
<tr>
<td>GS110minC2</td>
<td></td>
<td>Microwave heating for 110 min and carbonation for 2h</td>
</tr>
<tr>
<td>LS70min</td>
<td></td>
<td>Microwave heating for 70 min</td>
</tr>
<tr>
<td>LS70minC2</td>
<td></td>
<td>Microwave heating for 70 min and carbonation for 2h</td>
</tr>
<tr>
<td>LS90min</td>
<td>35% limestone + 65% cement</td>
<td>Microwave heating for 90 min</td>
</tr>
<tr>
<td>LS90minC2</td>
<td></td>
<td>Microwave heating for 90 min and carbonation for 2h</td>
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<td>Microwave heating for 110 min</td>
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<tr>
<td>LS110minC2</td>
<td></td>
<td>Microwave heating for 110 min and carbonation for 2h</td>
</tr>
</tbody>
</table>
7.3.3 Carbonation behaviour of the raw materials

As the mineral additions also have certain carbonation reactivity which may affect the CO_2 uptake and compressive strength in the subsequent experiments (Monkman and Shao, 2006), the carbonation behaviour of the fly ash and GGBS were assessed in this project. Limestone powder is considered to be inert at the very early age of hydration. The fly ash and GGBS (with no addition of cement) were exposed to CO_2 at 5 bar pressure for 2 hours with appropriate amount of water (water content high enough for the carbonation reaction but not too high to impede the reaction). To be more precise, the w/c ratio was 0.15 for GGBS and 0.2 for fly ash. The w/c ratio is determined by preliminary experiment and also referenced to the study by Monkman and Shao (Monkman and Shao, 2006).

The XRD patterns for fly ash and GGBS before carbonation (BC) and after carbonation (AC) are shown in Figure 7.1. The XRD analysis in Figure 7.1(a) confirms a glassy structure in the fly ash by the hump before carbonation. The main crystalline phases in the as-received fly ash were mullite, quartz and hematite. It seems that carbonation did not change the as-received fly ash, as the same XRD patterns were shown with no peak for calcite or any other carbonated form product. This disagrees with the results in the study (Monkman and Shao, 2006) where calcite was formed after carbonation. This may be caused by the different amount of CaO in the as-received fly ash, with the value of 2.31% in our project (as seen in Chapter 4) but 29.6% in the reference (Monkman and Shao, 2006).

Figure 7.1(b) gives the XRD patterns of the as-received and carbonated GGBS. The figure also shows a glassy structure in the as-received material, as well as the pre-existing calcite, quartz and β-C_2S. The intensity of the peak for calcite increased significantly at 2θ = 29.4° after carbonation, which may result from the carbonation of β-C_2S (Young et al., 1974, Shtepenko et al., 2006).
In summary, the as-received fly ash in this project was inert to CO$_2$, but the GGBS could be carbonated. Then TG analysis was performed to determine the degree of carbonation of GGBS.

TG/DTG curves of GGBS before and after carbonation are shown in Figure 7.2. Based on the weight loss of TG curves from 500°C to 726°C, associated with the decomposition of CaCO$_3$, it can be calculated that the CO$_2$ uptake of GGBS increases by 1.72% (from 0.16% to 1.88%) after carbonation, suggesting 1.72% CO$_2$ was absorbed with respect to GGBS mass. The amount of CO$_2$ absorbed was relatively low when considering nearly 40% CaO is present in the GGBS from the XRF analysis (in Chapter 4), indicating the majority of calcium remained inert to CO$_2$. The DTG peak for C-S-H gel centred at 130°C increased considerably, confirming the formation of C-S-H gel after carbonation. The increased C-S-H peak may be also attributed to the carbonation of β-C$_2$S (Young et al., 1974, Shtepenko et al., 2006).
Figure 7.2 TG/DTG analysis of as-received and carbonated GGBS
7.3.4 Effects of microwave-based preconditioning on the setting time of mortar containing different mineral additions

The setting times of mortar samples are determined by the penetration resistance described in the Chapter 4. The penetration resistance values of 3.5 MPa and 27.6 MPa are related to the initial setting and final setting, respectively (ASTM, 2008). As concluded from Chapter 5, the final setting time is close to the threshold preconditioning time, which is 70 min for the MP sample. As the final setting times are reported to be delayed with the mineral additions, the start preconditioning time is 70 min for all the samples containing mineral additions (Naik and Singh, 1997, Brooks et al., 2000, Özbay et al., 2016). Table 7.2 shows the penetration resistance of mortar samples after different microwaving times. The penetration resistance increased with preconditioning time. In addition, for the FA and GS samples, the final setting time is close to 90 min and for the LS sample, the final setting time is close to 70 min. It should be noted that penetration resistance is out of range shortly after the final setting time.

Table 7.2 Effects of mineral additions on the penetration resistance of mortar subjected to microwave-based preconditioning

<table>
<thead>
<tr>
<th>Penetration resistance (MPa)</th>
<th>70 min</th>
<th>90 min</th>
<th>110 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>8.34</td>
<td>24.9</td>
<td>38.92</td>
</tr>
<tr>
<td>GS</td>
<td>15.4</td>
<td>32.7</td>
<td>/</td>
</tr>
<tr>
<td>LS</td>
<td>28.2</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

Naik and Singh (1997) studied the effects of the replacement ratio of cement with four types of fly ash in concrete at ambient temperature, and found that the addition of 30% fly ash delayed the final setting time by 3.5h ~ 7h when compared to the pure PC concrete. Brooks et al. (2000) found that the addition of 30% fly ash and 40% GGBS delayed the final setting time by around 4h and 10h, respectively. The study by Barnett (2006) showed that the GS mortar exhibited lower early strength than the pure PC mortar, but had a higher increase rate of early strength than the pure PC mortar at elevated
temperatures. With the temperature feedback control system in microwave heating, Sohn (1999) found that when cured at 60°C, the pure PC mortar reached the penetration resistance of 13 MPa at 73 min. With the same curing temperatures, the addition of 50% GGBS and 20% fly ash delayed the time, and reached the penetration of 13 MPa at 88 min and 89 min, respectively. In summary, the addition of fly ash and GGBS delayed the setting time of mortar or concrete significantly, but the delay time was shortened at elevated temperatures. The references are consistent with the results in this project. The setting times were delayed for 20 min with the addition of fly ash and GGBS at an elevated temperature of 70°C.

By contrast, the limestone powder can have different effects on the setting times. The study by Bentz et al. (2017) showed that the addition of limestone powder in cement with a replacement ratio less than 40% had little impact on setting time; however, a higher replacement ratio delayed the setting time. The limestone powder has two-fold effects on the setting times. On the one hand, the limestone powder provides nucleation sites and accelerates the hydration. On the other hand, the diluting effect of the limestone powder retards hydration. In this project, with 35% limestone powder and at elevated temperature, the setting time of the mortar was unchanged in comparison to the pure cement mortar.

In summary, the final setting time for the FA and GS mortars are 90 min, while for the LS sample is 70 min. Then the three time points close to the final setting times of the mortar (70 min, 90 min, 110 min) were selected to study the threshold preconditioning time for the subsequent carbonation curing.
7.3.5 Effects of fly ash on the compressive strength development and carbonation efficiency of mortar subjected to the microwave-based preconditioning and carbonation curing

7.3.5.1 Effects of fly ash on the compressive strength before and after carbonation

The increase ratio is defined as the ratio of compressive strength after carbonation to that before carbonation. The effect of fly ash on the compressive strength of mortar subjected to different preconditioning times before and after carbonation is shown in Figure 7.3. The strength of mortar after carbonation was 3.3 MPa at 70 min preconditioning but more than doubled with 8.72 MPa recorded at 90 min preconditioning; however, a further preconditioning of 20 min (110 min) only slightly increased the carbonated compressive strength to 9.72 MPa. It was found that the increase ratio peaked at 90 min, thus 90 min was considered as the threshold preconditioning time of fly ash blended PC mortar.

![Figure 7.3 Effects of fly ash on the compressive strength of mortar at different preconditioning time](image-url)
7.3.5.2 Effects of fly ash on the carbonation efficiency

The CO\textsubscript{2} uptake and depth of carbonation were analysed to assess the carbonation efficiency of mortar after different microwave-based preconditioning times. It can be seen from Figure 7.4 that the CO\textsubscript{2} uptake has increased from 10.7\% to 14.2\% as the preconditioning time increased from 70 min to 90 min, and further increased to 15.6\% at 110 min. These results show that the degree of carbonation is higher with longer preconditioning times, with the most significant increase between 70 min and 90 min.

![Figure 7.4 Effects of fly ash on CO\textsubscript{2} uptake of mortar at different preconditioning time](image)

The effect of fly ash on the carbonation front was assessed by spraying phenolphthalein solution, as presented in Figure 7.5. The penetration depth was much higher with preconditioning time increasing from 70 min to 90 min, which was associated with the sharp increase in compressive strength and CO\textsubscript{2} uptake in the same time period. However, with 20 min further preconditioning (110 min), there was no significant change in the carbonation depth of the mortar samples. The samples at 110 min preconditioning were carbonated more advanced than that at 90 min preconditioning as indicated by clearer edge of the carbonated zone.

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7.3.6 Effects of GGBS on the compressive strength development and carbonation efficiency of mortar subjected to the preconditioning and carbonation curing

7.3.6.1 Effects of GGBS on the compressive strength before and after carbonation

The effect of GGBS on the compressive strength of mortar subjected to different preconditioning times before and after carbonation is shown in Figure 7.6. A similar pattern was observed in the GS mortar as that in the FA mortar, with the increase ratio peaking at 90 min (9.68). The compressive strength of mortar after carbonation increased steadily from 8.12 MPa at 70 min to 16.63 MPa at 90 min, with a further increase to 19.16 MPa at 110 min.
7.3.6.2 Effects of GGBS on the carbonation efficiency

Figure 7.7 shows the CO$_2$ uptake of a mortar containing GGBS after the microwave-based preconditioning and carbonation regime. The CO$_2$ uptake obtained after a preconditioning time of 70 min and 2h carbonation was 11.2%, while with preconditioning times of 90 min and 110 min and 2h carbonation curing was 15.2% and 16.3%, respectively. The CO$_2$ uptake achieved in the GS sample is generally higher (11.2% ~ 16.3%) than that in the FA sample (10.7% ~ 15.6%). This is likely because the GS can be carbonated (1.72% of CO$_2$ uptake) as shown in Section 7.2.3, while the FA is almost inert to CO$_2$. 

Figure 7.6 Effects of GGBS on the compressive strength of mortar at different preconditioning time
The carbonation front for the mortar containing GGBS was detected by phenolphthalein spray after microwave-based preconditioning and carbonation, as can be seen in Figure 7.8. A noticeably deeper penetration depth was observed in the mortar with increased preconditioning from 70 min to 90 min, along with a large strength gain and an increased CO$_2$ uptake. By comparison, a further preconditioning to 110 min did not give a deeper carbonation depth. As a result, the 90 min preconditioning time was deemed to be the threshold preconditioning time for mortar containing 35% GGBS.

Figure 7.7 Effects of GGBS on CO$_2$ uptake of mortar
7.3.7 Effects of limestone powder on the compressive strength development and carbonation efficiency of mortar subjected to the preconditioning and carbonation curing

7.3.7.1 Effects of limestone powder on the compressive strength before and after carbonation

Figure 7.9 shows the effect of limestone powder on the compressive strength of mortar subjected to different preconditioning times before and after carbonation. While the compressive strength before carbonation showed an increase from 2.12 MPa at 70 min to 6.63 MPa at 110 min, there was less change in the strengths after carbonation, which were in the range from 12.78 MPa to 14.58 MPa. Consequently, the increase rate dropped with preconditioning time, from 6.02 at 70 min to 3.49 at 90 min then 2.15 at 110 min.
7.3.7.2 Effects of limestone powder on the carbonation efficiency

Figure 7.10 shows the CO$_2$ uptake of a mortar containing 35% limestone powder subjected to different microwave-based preconditioning times and carbonation curing. For a preconditioning time of 70 min, the CO$_2$ uptake was 13%, and reached 14.8% and 15.9% with preconditioning for 90 min and 110 min, respectively.
The carbonation depth of the limestone mortar after carbonation curing is presented in Figure 7.11. The carbonation depth of the mortar did not change significantly when preconditioning time increased from 70 min to 110 min. The depth in carbonation curing correlates with the strength development, which also saw less increase in carbonated strength with longer preconditioning time. Therefore, preconditioning time for 70 min was taken as the threshold duration.

Figure 7.10 Effects of limestone on carbonation uptake of mortar

Figure 7.11 Effects of limestone powder on carbonation profile of mortar at preconditioning time (a) 70 min (b) 90 min (c) 110 min
In summary, the microwave-based preconditioning and carbonation regime can be applied to the mortar samples containing mineral additions, as significant improvement in the compressive strength and increase in the CO$_2$ uptake were observed. The threshold preconditioning time for fly ash and GGBS was 90 min, while for limestone was 70 min. These preconditioning times will be used for each mineral addition afterwards.

7.3.8 Effects of mineral additions on the water distribution of mortar samples subjected to the threshold microwave-based preconditioning time

The water distribution of the mortar samples subjected to the threshold microwave-based preconditioning time was measured. Similar to the Chapters 5 and 6, water was divided into four types of water: evaporated water 1, water lost during preconditioning; evaporated water 2, water lost after heating but prior to the carbonation process; combined water, water combined in the hydration products and the remaining water.

Figure 7.12 shows the water distribution of samples with different additions subjected to the threshold preconditioning time determined above. The MP and LS samples were preconditioned for 70 min, with 61.53% and 64.58% of the total water left respectively. When the FA and GS samples were preconditioned for 90 min, only 58.15% and 57.98% of the total water remained. A longer preconditioning time led to higher amount of evaporated water and thus less remaining water; the evaporated water for FA and GS samples (evaporated water 1 + evaporated water 2) was around 37% but for MP and LS samples they were only 31% and 26%, respectively, which shows the water loss is more influenced by the preconditioning time. It was interesting to note that the amount of combined water was reduced with FA and GS due to the dilution of cement, which agrees with the previous studies (Lam et al., 2000, Wang et al., 2016), but the combined water for LS was even higher than that for the pure cement mortar, suggesting the nucleation sites introduced by limestone powder significantly increased the hydration (Bentz et al., 2017, Moon et al., 2017).
Figure 7.12 Water distributions of samples with mineral additions subjected to threshold preconditioning time

7.3.9 Effects of the mineral additions on the carbonation profiles of mortar samples subjected to the threshold microwave-based preconditioning time

The carbonation profiles of the mortar samples containing mineral additions subjected to the threshold preconditioning times and carbonation are presented before, and then compared in Figure 7.13. The carbonation depths all increased in comparison to the MP sample. As described in the previous chapters, the
rate of carbonation reaction mainly depends on the transport of CO$_2$. With a set CO$_2$ pressure and carbonation time, the transport of CO$_2$ is influenced by the remaining water content and the permeability of samples. With the threshold water content (influenced by microwave-based preconditioning time), the permeability of samples is the primary factor that influences the degree of carbonation. However, at early stage, the additions were mostly unreacted and thus would increase the permeability.

In the study by Wang et al. (2016) where 40% fly ash and GGBS replaced cement, the fly ash did not react in the first 2 days and the GGBS had a reaction degree of only 6.74% in the first day at ambient temperature. Ye et al. (2007) showed that the limestone powder was not involved in the chemical relations at early age. In the study by Zhang et al. (2016) where air preconditioning for 10.5h was applied in the paste and concrete samples containing 0%, 20% and 50% fly ash before carbonation curing, the reaction degree of fly ash was less than 1% for the 20% and 50% blended cement paste after preconditioning. In the same study, the CO$_2$ uptake increased significantly with the addition of fly ash. After 24h carbonation, the CO$_2$ uptake for pure PC paste was 19.57%, but increased to 24.10 and 28.20% with the addition of 20% and 50% fly ash, respectively. Seo et al. (2018) used 5% atmospheric CO$_2$ concentration to carbonation-cured samples containing 0%~ 50% volcanic fly ash for 28d, and found that the CO$_2$ uptake increased with the percentages of volcanic ash. The addition of limestone powder was also found to increase the CO$_2$ uptake either without preconditioning (initial low water content) (Tu et al., 2016) or with preconditioning (initial high water content) (Shao et al., 2014). This was attributed to the nucleation sites provided by the limestone powder, and could also be attributed to the increased permeability caused by the inert particles (limestone powder is considered to be inert at early stage of hydration).

In this project, microwave-based preconditioning lasted for 70 ~ 90 min, which is expected to result in a lower reaction degrees of the FA, GS and LS mortar samples when compared with the literatures (Zhang et al., 2016, Wang et al., 2016, Ye et al., 2007). As a consequence, the permeability can be increased
with the additions and the CO$_2$ uptake and carbonation depth can also be increased accordingly.

![Figure 7.13 Carbonation profiles of mortar samples subjected to threshold preconditioning time](image)

**Figure 7.13** Carbonation profiles of mortar samples subjected to threshold preconditioning time

### 7.3.10 Summary

The threshold preconditioning time is close to the final setting time of the mortar samples containing additions, which is in agreement with the conclusion in Chapter 5.
After the microwave-based preconditioning and carbonation curing for 2h, the compressive strengths of all the mortar samples containing additions were lower in comparison to the pure cement mortar sample (see in Chapters 5 and 6). This may be due to the dilution effect of the relatively inert mineral addition in comparison to cement (Zhang et al., 2016, Tu et al., 2018, Agarwal, 2015). In addition, the mortar samples containing additions have a higher CO₂ uptake and carbonation depth than the pure cement mortar.
7.4 The microstructure and the reaction products of PC blends subjected to the threshold microwave-based preconditioning time and carbonation curing

7.4.1 Microstructure of the mortar samples

7.4.1.1 SEM images

The changes in the morphology of the MP sample before and after carbonation curing are shown in Figure 7.14 (a) and (b). Before carbonation, there were obvious CH crystals and fibrous C-S-H gel present. After carbonation, there were presence of CaCO$_3$ and sheet-like C-S-H gel, which may be due to the carbonation of the CH, C-S-H gel and unreacted clinker phases.

The morphology of FA mortar samples before and after carbonation are in Figure 7.14(c) and (d). Before carbonation, Figure 7.14 (c) shows the hydration products with C-S-H gel and AFt phases. These phases disappeared after carbonation as seen in Figure 7.14 (d), similar to that in the MP sample.

Figure 7.14(e) shows the morphology of mortar with GGBS before carbonation. Compared to the FA sample, the particles were connected with gels, which appears to show the partial hydration of GGBS. After carbonation (Figure 7.14(f)), the GGBS particles were covered with C-S-H gel that was intermixed with CaCO$_3$.

The limestone particles are covered with the hydration products before carbonation, as seen in Figure 7.14(g), which clearly shows the nucleation effect. In Figure 7.14(h), there are cubic crystals (calcite) on the fractured surface, suggesting the nucleation effects for the carbonation reaction.
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(a) MP70min

(b) MP70minC2h

(c) FA90min

(d) FA90minC2h

(e) GS90min

(f) GS90minC2h
### 7.4.1.2 BSE images

Figure 7.15 shows the BSE images of polished mortar samples containing fly ash and GGBS before and after carbonation, with EDS spectrum of points shown in Table 7.3. The clinker phases were identified as ‘C’ for C\textsubscript{3}S, C\textsubscript{2}S, C\textsubscript{3}A and C\textsubscript{4}AF, ‘F’ for fly ash and ‘S’ for ‘GGBS’ (Winter, 2012). After 90 min of microwave-based heating, the majority of fly ash remains unreacted (Figure 7.15(a)). After 2h carbonation, the porosity was noticeably reduced. The reduction of porosity is considered to be mainly related to the carbonation of cement particles rather than the fly ash particles, because the fly ash particles have retained the same spherical shape, as seen in Figure 7.15(b). In addition, the C-S-H layer on the surface of the fly ash was carbonated, which resulted in a C-S-H gel with a low Ca/Si ratio (Figure 7.15(b)). The EDS analysis of point 2 shows the original composition of fly ash, with a Ca/Si ratio of 0.19 (Table 7.3). On the surface of the particles, the Ca/Si ratio of 0.4 in point 1 is higher (Table 7.3), suggesting the produced C-S-H gel was carbonated.

The BSE images of the GGBS mortar before and after carbonation are shown in Figure 7.15 (c) and (d). After carbonation, the porosity of the GGBS mortar was also lower than that before carbonation due to the carbonation of cement particles. In addition, the porosity appeared to be lower compared to the
carbonated fly ash mortar, which is also likely due to the carbonation of GGBS particles, as demonstrated in Section 7.3.3. This can also explain the higher compressive strength of the GS mortar (16.63 MPa) than the FA sample (8.72 MPa) after 90 min preconditioning and 2h carbonation, as seen in Sections 7.3.5 and 7.3.6. From the EDS ratios shown in point 3 (Table 7.3), the Ca/Si ratio shows the original composition of as-received GGBS (Ca/Si ratio of 1.08). The Ca/Si ratio of GGBS (1.08) is higher than that of fly ash (0.19); in addition, GGBS undergoes a temperature history which is sufficiently high to form calcium silicates (Section 7.3.3). This may be the reason why the GGBS is more reactive than fly ash. The Ca/Si ratio of C-S-H produced in the matrix was high (4.22), which is higher than the conventional C-S-H gel (~ 1.7). This may be due to an intermixed C-S-H gel and CaCO₃, as explained in Chapter 5.
Table 7.3 EDS analysis of BSE images of fly ash mortar and GGBS mortar

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<tr>
<th>Points</th>
<th>Ca</th>
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<td>0.63</td>
<td>0</td>
<td>4.22</td>
</tr>
</tbody>
</table>

7.4.2 Reaction products of the paste samples

Paste samples were prepared to avoid the influence of sand in the mortar samples. Powder samples after carbonation were drilled from the top 0-2 mm, which represents the highly carbonated layer. The reaction products were investigated with XRD and TG.

(1) XRD

Figure 7.16 shows the reaction products before and after carbonation in samples containing additions. The carbonation of the cement paste has been described in Chapters 5 and 6 (Figure 7.16 (a)). Carbonation curing consumes calcium silicates, CH and AFt, forming calcite and C-S-H gel (Zhu et al., 2018, Tu et al., 2018, Sharma and Goyal, 2018). These changes were also seen in all three samples containing mineral additions (Figure 7.16 (b), (c) (d)), which demonstrates that the carbonation of cement is the primary reaction. Calcite is the main carbonation products of all samples, with small peak of aragonite observed in CE70C2, FA90C2 and GS90C2 but not in LS70C2. This may be explained that the calcite polymorph of the limestone powder serves as the nucleation sites, producing calcite as well.
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Figure 7.16 Effects of mineral additions on reaction products before and after carbonation

(2) TG/DTG

Figure 7.17 shows the TG/DTG curves of paste samples containing different mineral additions both before and after carbonation. The curves for the pure cement paste show an increased peak for CaCO₃, and decreased peaks for C-S-H gel and CH. Similar patterns were observed in the paste samples containing mineral additions. For the LS sample, the TG curve shows a much higher peak for the decomposition of CaCO₃ when compared with other groups.
Figure 7.17 TG/DTG curves of samples with different additions before and after carbonation

The TG data of paste samples containing mineral additions before and after carbonation are shown in Table 7.4. The weight loss can be obtained directly from the TG data. The weight loss (105 ~ 400 °C) related to C-S-H gel is attributed to amount of H$_2$O bound in the gel. The weight loss (400~ 500 °C) related to CH is due to the H$_2$O combined, and the amount of CH was calculated using Eqs. 7.1 and 7.2. The weight loss related to CaCO$_3$ is due to the CO$_2$ weight loss, which is normalised to cement mass in the samples containing mineral additions. The calculation of CO$_2$ uptake (%) is calculated using Eq. 7.3 (for the MP sample) and 7.4 (for the FA, GS and LS sample).

\[
Ca(OH)_2 \rightarrow CaO + H_2O \quad (7.1)
\]

\[
\begin{align*}
74 \text{ g/mol} & \quad 56 \text{ g/mol} & \quad 18 \text{ g/mol}
\end{align*}
\]
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\[
%CH = %H_2O \times \frac{74}{18} \tag{7.2}
\]

\[
%CO_2 \text{ uptake} = %CO_2 \text{ amount }_{\text{after carbonation}} - %CO_2 \text{ amount }_{\text{before carbonation}} \tag{7.3}
\]

\[
%CO_2 \text{ uptake} = \frac{( %CO_2 \text{ amount }_{\text{after carbonation}} - %CO_2 \text{ amount }_{\text{before carbonation}} )}{0.65} \tag{7.4}
\]

The CH was completely consumed in the carbonation reaction (as seen from the XRD and TG results), so the amount of CH after carbonation is 0, which is not shown in the Table. The table shows that the MP sample had a higher amount of C-S-H gel (1.59%) than the FA sample (1.15%) and the GS sample (1.33%) before carbonation. This is mainly due to the dilution effect of the mineral additions. In addition, the lower amount of C-S-H gel for the FA sample than the GS sample may be explained that fly ash had a lower reaction degree than GGBS (also indicated from a higher CH content in the fly ash sample). These are in line with the results investigated by Wang et al. (2016). The study showed that when 40% fly ash and GGBS replaced cement, the fly ash did not react in the first 2 days and the GGBS had a reaction degree of only 6.74% in the first day at ambient temperature. The reaction degrees increased to 6.23% and 20.21% with constant curing for 1d at 50 °C. In this study, the duration of microwave heating was only 90 min, which was difficult to activate fly ash particles but may result in a low reaction degree of GGBS particles. The hydration of GGBS particles can be seen in the Figure 7.14 (e). The highest amount of C-S-H gel (2.20%) and CH (4.82%) were observed in the LS sample, which further demonstrates the accelerated hydration of the limestone powder due to its nucleation effects (Moon et al., 2017, Bentz et al., 2017).

As also shown in Table 7.4, for the MP sample, a net increase of 12.14% CO₂ uptake (by mass of the cement) was observed. However, the CO₂ uptake for the samples containing mineral additions ranged from 14.38% to 16.5%, showing a higher CO₂ uptake. As discussed in Section 7.2.9, the limited microwave-based preconditioning times (70 ~ 90 min) was expected to result in a reaction degrees of the fly ash, GGBS and almost inert limestone powder.
Therefore, the permeability is expected to be higher when compared to the samples with the additions and thus the CO$_2$ uptake can be increased.

The GS sample had a higher CO$_2$ uptake (16.5%) than the FA and LS samples (14.38% and 14.97%, respectively). The reason can be explained by the fact that the GS itself can be carbonated. The GS alone absorbs 1.72% CO$_2$, as shown in section 7.3.3.

Compared with the CO$_2$ uptake for the MP sample (12.14%), the figure for the LS sample was higher (14.97%). These results corroborate with the previous studies (Tu et al., 2016, Tu et al., 2018). In those studies, 5% ~ 50% limestone powder replaced cement in the paste samples, which significantly increased the CO$_2$ uptake. The studies attributed the increased CO$_2$ uptake to both the increase in the CO$_2$ transport and the nucleation sites produced by limestone powder for the carbonation reaction. However, in this project, the CO$_2$ figure for the LS sample was only slightly higher than that for the FA sample (14.38%). As the fly ash sample was much coarser than the limestone powder (shown in Chapter 4), the nucleation effects from the fly ash particles are weak. Therefore, it appears that that the increased CO$_2$ transport may be the primary reason for the increased CO$_2$ uptake in the samples containing mineral additions.

Table 7.4 TG data of the cement paste and paste samples containing mineral additions before and after carbonation curing

<table>
<thead>
<tr>
<th>Paste samples</th>
<th>Before carbonation</th>
<th>After carbonation</th>
<th>Net increase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%H$_2$O from C-S-H</td>
<td>%CH</td>
<td>%CO$_2$ amount</td>
</tr>
<tr>
<td>MP</td>
<td>1.59</td>
<td>3.01</td>
<td>2.21</td>
</tr>
<tr>
<td>FA</td>
<td>1.15</td>
<td>2.58</td>
<td>1.94</td>
</tr>
<tr>
<td>GS</td>
<td>1.33</td>
<td>1.92</td>
<td>1.43</td>
</tr>
<tr>
<td>LS</td>
<td>2.20</td>
<td>4.82</td>
<td>16.02</td>
</tr>
</tbody>
</table>
7.5 Evolution of the compressive strength, microstructure and reaction products of the PC blends over time

7.5.1 Introduction

The carbonation reaction consumes calcium silicates and then forms calcium carbonates on the surface of calcium silicates. Thus, further hydration might be impeded because the dissolution of calcium silicates is difficult. In addition, the carbonation reaction reduces the alkalinity in the samples so the reaction degrees of GGBS and fly ash, which is supposed to occur in the long term, may be affected. Therefore, the 28d strength was assessed to evaluate the influence of carbonation on the further hydration of cement, GGBS, fly ash and limestone powder. The microstructure of the mortar and reaction products of paste samples were characterized with SEM and XRD/TG.

7.5.2 Evolution of compressive strengths of mortar with different types of mineral additions over time

To make the comparison clear in the subsequent sections, the sample subjected to preconditioning and 2h normal hydration is denoted as ‘PN’, the sample subjected to preconditioning and 2h carbonation curing is denoted as ‘PCC’. After preconditioning, they were sealed and placed in the curing room for different hydration times.

Figure 7.18 shows the evolution of compressive strengths of mortars with different types of mineral additions at different times. All four samples in Figure 7.18 show a great increase in strength of the PCC sample compared to the PN sample at 4h, due to the carbonation reaction (Zhu et al., 2018, Tu et al., 2018, Agarwal, 2015). But the gap in strength between the PCC sample and PN sample narrowed after 1d and 28d, because the ongoing strength development in the PN sample was more rapid between 1d and 28d. In addition, the mortars containing mineral additions all showed a lower strength than the pure cement mortar at all ages. This is in agreement with previous studies where concrete containing mineral additions showed a lower strength than the pure cement
concrete after being subjected to carbonation curing (Tu et al., 2018, Sharma and Goyal, 2018, Seo et al., 2018a, Guo et al., 2018, Zhang et al., 2016). The decrease in strength may be attributed to the dilution effect of additions.

More specifically, the values of the compressive strength of the pure cement mortar at 4h were 6.72 MPa and 27.56 MPa in the PN sample and PCC sample, respectively (Figure 7.18 (a)). From 4h to 1d, the strength increase for the PN sample was rapid but the increase for the PCC sample was relatively slow; they finally reached a similar value of about 32 MPa. The strengths continued to increase with time, with the PN sample reaching a strength of 55.8 MPa at 28d, and the PCC sample obtaining a slightly lower strength of 54.4 MPa at the same time. For the mortar with fly ash (Figure 7.18(b)), the gap between the PN and PCC samples was large at 4h as well, and both samples exhibited rapid increase in strength at 1d. The PCC sample demonstrated significantly higher strength at 1d than the PN sample, with 19.76 MPa and 13.92 MPa recorded, respectively. The situation reversed at 28d, the value of the PN sample was 39.2 MPa, compared to 34.6 MPa in the PCC sample. This is in agreement with the study by Zhang et al. (2016) that the fly ash concrete subjected to carbonation curing suffered a long-term strength loss in comparison to the hydrated concrete samples. They concluded that the pozzolanic reaction was weakened by carbonation curing.

A similar trend was observed in the mortar with GGBS (Figure 7.18(c)), with a higher strength in the PCC sample at 4h and 1d. But the 28d strength for the PCC sample was similar to that for the PN sample. This is in agreement with the study (Agarwal, 2015) where similar strengths between the carbonated and hydrated samples were observed in the GS mortar after 28d further hydration. The PCC sample with limestone powder exhibited a higher compressive strength than the PN sample at all ages (4h, 1d and 28d) in the mortar (Figure 7.18(d)). The gap was the largest at 4h and smaller at 1d and 28d. It should be noted that the LS mortar was the only composition that the PCC sample showed a higher strength than the PN sample at 28d. This may be explained that the all mineral additions increase the carbonation depth and degree of carbonation in the mortar sample compared to the pure cement mortar, which
enhances the compressive strength at 4h. Compared with the pure cement mortar, the LS sample continued the trend and showed a better mechanical strength even after 28d. Among the mortar samples containing mineral additions, the LS mortar is least affected by the lowered alkalinity caused by carbonation curing (Rostami et al., 2011), because the limestone powder does not undergo reactions with alkaline activators as fly ash and GGBS.
(a) MP Mortar

(b) FA mortar
Figure 7.18 Evolution of compressive strengths of mortar containing different additions

(c) GS mortar

(d) LS mortar
7.5.3 Evolution of the microstructure of mortar with different types of additions over time

After preconditioning and 2h carbonation curing, the mortar samples were sampled immediately (4h) or subjected to 28d hydration (28d). Two layers were taken from the mortar samples. A layer was cut from the top 0-10 mm, representing the highly carbonated layer, and a second layer was cut at a depth of 25-35 mm, representing the uncarbonated layer. Only the centre part of each layer was taken for characterisation to avoid the influence of carbonation on the sides.

Figure 7.19 presents the SEM images of the fractured surface of the different layers of the pure mortar at 4h and 28d. The appearance of C-S-H gel in the top layer of carbonated mortar both at 4h and 28d was very similar; in addition, little CH or newly produced C-S-H gel were present both at 4h and 28d. The cement particles seem to be covered by the CaCO₃ produced which impedes their further hydration. This is different from the study by He et al. (2016) where the unreacted cement particles continued to hydrate in the carbonated concrete. However, the study did not provide details about the depth of the samples in concrete, and the changes in morphology due to further hydration could occur in the deeper layer which was less affected by carbonation curing. By comparison, more changes are seen in the appearance of the C-S-H in the deeper layer between 4h and 28d (Figure 7.19 (c) and (d)). Conventional C-S-H gel was observed at 4h, but this became denser at 24h, which shows further hydration of cement particles (H.F.W.Taylor, 1997). This suggests that in the top layer, the high degree of carbonation impedes future hydration, but in the uncarbonated layer which is less affected by the carbonation reaction, hydration continues.
Figure 7.19 SEM images of the cement paste (MP) mortar at different ages

Similar phenomena are found in the samples containing all three additions (Figures 7.20, 7.21 and 7.22). Less change in the morphology of the highly carbonated layer was found, which suggests little further hydration of cement and reactions of additions. The cement and mineral addition particles were coated by a layer of CaCO$_3$. The coating probably prevents the dissolution of cement and mineral additions, thus influencing the cement hydration and reactions of fly ash and GGBS (Zhang et al., 2016). A more compact structure is observed in the second layer with longer hydration time, accompanied by a higher degree of hydration of the cement, fly ash and GGBS.
Figure 7.20 SEM images of the Fly ash (FA) mortar at different ages
Figure 7.21 SEM images of the GGBS (GS) mortar at different ages

(a) carbonated 4h (top)  
(b) carbonated 4h (second)  
(c) carbonated 28d (top)  
(d) carbonated 28d (second)
Figure 7.22 SEM images of the limestone powder (LS) mortar at different ages

7.5.4 Evolution of the reaction products of cement paste containing mineral additions over time

To avoid the influence of sand in mortar, paste samples were prepared. As stated earlier, the sample subjected to preconditioning and 2h normal hydration is denoted as ‘PN’, the sample subjected to preconditioning and 2h carbonation curing is denoted as ‘PCC’. They were sealed and placed in the curing room for different hydration times. For example, if the sample is subjected to microwave-based preconditioning for 90 min and then normal hydration for 2h, then it is
denoted as ‘PN-4h’. The sample subjected to microwave-based preconditioning and 2h carbonation, and then further hydration for 28d is denoted as ‘PCC-28d’.

For each paste sample, two layers were drilled from the top 0-2 mm and the top 6-8 mm which represent the highly carbonated layer and semi-carbonated layer, respectively. The reaction products that subjected to different further hydration times were characterized with XRD and TG.

(1) XRD

Figure 7.23 shows XRD patterns of the cement pastes with the different types of mineral additions at 4h and 28d. The XRD patterns of pure cement paste are shown in Figure 7.23(a). After 28d further hydration in the PN sample, the CH and AFt peaks increased, accompanied by a reduction in the peaks for calcium silicates, suggesting a significantly increased degree of hydration in the PN sample. This is a normal hydration process and has been widely studied in the literatures (Neville, 2011). By contrast, in the PCC sample at 4h, no peaks for CH or AFt were seen in both the highly carbonated layer (top 0-2 mm) and the semi-carbonated layer (top 6-8 mm). After 28d hydration, CH and AFt were still absent in the highly carbonated layer but present in the semi-carbonated layer. This shows that little further hydration has occurred in the highly carbonated layer with some hydration observed in the semi-carbonated layer. The results are consistent with the conclusion from the SEM images that little hydration was observed in the highly carbonated layer. Previous studies (Rostami et al., 2011, He et al., 2016) also showed that the carbonation curing prevents further hydration because of the coating of CaCO$_3$ on the unreacted calcium silicates. However, in their studies (Rostami et al., 2011, He et al., 2016), after 28d hydration, the amount of CH and C-S-H were increased due to further hydration. In contrast, in this project, no XRD peak for CH was detected after 28 hydration. This may be explained that in the previous studies (Rostami et al., 2011, He et al., 2016), the degree of carbonation was lower (indicated from the presence of CH after carbonation curing), and thus the impediment of CaCO$_3$ coating to the hydration of calcium silicates was less significant.
Figure 7.23(b), Figure 7.23(c) and Figure 7.23(d) show the XRD patterns of FA, GS and LS paste at 4h and 28d. A similar trend occurs in the PN sample with higher peaks for CH and AFt at 28d, but those peaks were not observed in the highly carbonated layer and were small in the semi-carbonated layer of the PCC sample at 28d. This again shows little further hydration of unreacted calcium silicates has occurred in the highly carbonated layer, which are consistent with the SEM images. As there was no CH produced in the top layer, it was expected that there was no further reactions between the CH and fly ash or GGBS at 28d.

The monocarboaluminate is only detected in the PN-28d of the LS sample. This is in agreement with the previous studies that the fine limestone powder reacts with C₃A to form monocarboaluminate (Moon et al., 2017, De Weerdt et al., 2011). However, such phase was not detected in the MP, FA and GS samples where the CaCO₃ phase was produced via carbonation curing. This can be explained that the C₃A phase is coated by the CaCO₃ phase produced during the carbonation curing, and could not contact with water. As a consequence, the future reaction of C₃A cannot proceed.
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(a) The MP paste

(b) The FA paste
Figure 7.23 XRD patterns of cement paste containing mineral additions over time
(2) TG

The DTG curves of the pure cement paste and the paste samples containing mineral additions at 4h and 28d are presented in Figure 7.24. Figure 7.24(a) shows the DTG curve of pure cement paste. Generally, the paste samples without carbonation (the PN samples) exhibited a significantly higher hydration degree at 28d than that at 4h, as seen from the increased peaks for C-S-H gel and CH. The paste sample with carbonation also showed a higher degree of hydration at 28d than that at 4h, but at a much lower rate. This agrees with the XRD results that the carbonation reaction prevents further hydration.
(a) The MP sample

(b) The FA sample
Figure 7.24 DTG analysis of cement paste containing mineral additions at different ages
The water loss from the dehydration of C-S-H gel reflects the changes in the amount of C-S-H gel. Figure 7.25 shows the water loss (105 ~ 400 °C) from the paste samples containing mineral additions at 4h and 28d. The C-S-H gel could be depolymerised in the carbonation process (Shao et al., 2014), as seen in the LS sample where a lower amount of water loss in the carbonated top 0-2 mm layer than the hydrated sample was observed at 4h. However, more C-S-H gel could also be produced due to the carbonation of calcium silicates (Shao et al., 2014). As a consequence, the MP, FA and GS samples showed a higher amount of water loss of C-S-H gel in the carbonated top 0-2 mm layer than the hydrated sample.

The PN-28d samples in all paste samples showed the highest amount of water loss in all samples due to cement hydration and further reaction of additions. For the PN-28d samples, the MP and GS samples had a comparable amount of water loss, showing that GGBS has a high reaction degree which is comparable with cement. This is followed by the FA sample (PN-28d), which can be explained that the fly ash generally has a lower reaction degree than the GGBS (Wang et al., 2016). The LS sample (PN-28d) has the lowest amount of water loss. Among the four samples at 4h (PN-4h), the LS sample has the highest amount of water loss. This can be explained that the LS sample can serve as the nucleation effects and accelerate hydration at early age (Moon et al., 2017, Bentz et al., 2017), but because the LS sample is mostly inert in the subsequent hydration process (though it can react with calcium aluminates in the long run) (De Weerdt et al., 2011), so the LS sample at 28d (PN-28d) shows the lowest amount of C-S-H gel after 28d hydration. This can explain that compared with other PN samples (the FA and GS samples), the PN of the LS mortar sample exhibited the lowest compressive strength after 28d hydration.

At 4h, all samples (the MP, FA, GS, LS samples) showed a slightly higher amount of water loss in the PCC-4h-top 6-8 mm layer than in the PCC-4h-top 0-2 mm layer. This may be explained that the consumption of C-S-H gel due to carbonation curing in the top 6-8 mm layer is less severe than that in the top 0-2 mm layer. However, all samples exhibited a higher amount of water loss in the PCC-28d-top 6-8 mm layer than in the PCC-28d-top 0-2 mm layer. This shows
that the top 6-8 mm layer did not impede the hydration as much as the top 0-2 mm layer.

The GS sample exhibited a higher amount of water loss than the FA sample in the PCC-4h-top 6-8 mm layer (3.11% and 2.74%, respectively). The situation reversed at 28d (4.64% and 5.54%, respectively). This shows that in the top 6-8 mm layer (semi-carbonated layer), GGBS is more sensitive to carbonation. This may be explained that the GGBS particles can carbonate as well, unlike the inert fly ash. As a consequence, the coating of CaCO$_3$ on the GGBS particles is another reason that prevents the further hydration of GGBS.

Figure 7.25 Water loss (105 ~ 400 °C) of the paste samples containing mineral additions
7.5.5 Summary

In summary, the compressive strengths of all the mortar samples continue to develop until 28d. However, the highly carbonated layer could not contribute to the strength development because the coating of CaCO$_3$ on cement pastes impedes further cement hydration and reactions of mineral additions. This can be observed from the unchanged SEM images and XRD patterns between the samples at 4h and 28d. In comparison, the samples that are less affected by the carbonation curing continue to develop strength through cement hydration and reactions of mineral additions. The LS sample without carbonation at 4h produces the highest amount of C-S-H gel, but the LS sample with carbonation at 4h produces the least amount of C-S-H gel due to the mostly inert limestone powder. The GS sample is more sensitive to carbonation curing compared with the FA sample.
7.6 Conclusion

This chapter has studied the effects of fly ash, GGBS and limestone powder on the properties, carbonation efficiency, and carbonation products of mortar and cement paste subjected to the microwave-based preconditioning and carbonation regime. The main conclusions can be summarized as follows.

- In comparison to the pure cement mortar, the threshold microwave-based preconditioning time was prolonged for the mortars containing the GGBS and fly ash but remained the same for the mortar containing limestone powder.
- Compared with the pure cement mortar, the compressive strengths of mortars decreased, but the CO$_2$ uptake and carbonation depths increased with the three types of additions after preconditioning and 2h carbonation.
- The main carbonation products remained the same when different additions were added to the paste, with calcite the predominant phase and aragonite the minor phase present. However, aragonite was not found in the mortar containing limestone powder.
- After microwave-based preconditioning, the limestone mortar sample subjected to preconditioning and carbonation curing was the only composite showing higher strength at 28d, the fly ash mortar sample with carbonation exhibited lower strengths, while equivalent strengths was found in the GGBS mortar.
- In all samples with or without additions, little further hydration was found in the highly carbonated layers in the long term. In contrast, hydration continues in the semi-carbonated and uncarbonated layers.
- The paste sample containing limestone powder without carbonation produces the highest amount of C-S-H gel at 4h, but produces the least amount of C-S-H gel at 28d due to the mostly inert limestone powder.
- The samples containing GGBS subjected to carbonation curing showed further impediment to future hydration when compared with the samples containing fly ash, which may be attributed to the coating of the CaCO$_3$ on the GGBS particles.
Chapter 8  Conclusions and Future work

8.1 Conclusions

Microwave-based preconditioning has been used prior to carbonation curing, and the results show a marked improvement in compressive strength can be achieved after only 2h carbonation with significant CO$_2$ uptake. Some specific conclusions can be made as follows.

8.1.1 Development of a suitable protocol for microwave-based preconditioning and accelerated carbonation curing

(1) Effects of preconditioning time

- Increasing the microwave-based preconditioning time up to the threshold time leads to a much higher degree of carbonation and related compressive strength. Further increasing the preconditioning time beyond the optimum shows little increase in carbonation efficiency or strength development. The optimum preconditioning time varies with w/c ratio being 70 min for samples with a w/c ratio of 0.37 and 90 min for samples with a w/c ratio of 0.5.
- The threshold preconditioning time is very close to the final setting time.
- The microwave-based heating proves to be a time-efficient preconditioning method due to its volumetric heating nature.

(2) Effects of carbonation time

- The carbonation depth of mortar increased significantly with carbonation time from 1h to 2h but exhibited little change when the carbonation time was further increased up to 24h. The increase in strength between 2h and 24h could be primarily attributed to the ongoing hydration in the uncarbonated layer. The threshold carbonation time is determined as 2h.
- The percentages of crystalline CaCO$_3$ and amorphous CaCO$_3$ change with carbonation time and are likely to be attributed to the different reaction rates of CH and C-S-H gel with CO$_2$. 
• Calcite is the predominant polymorph of crystalline CaCO$_3$, with aragonite only produced at high degrees of carbonation.

• The Ca/Si ratio of C-S-H gel in the matrix is expected to be reduced after carbonation, however, the Ca/Si ratio detected in the matrix is higher than that in the conventional C-S-H gel. This could be mainly attributed to the intermixed C-S-H gel and CaCO$_3$ produced.

(3) Effects of CO$_2$ pressure

• There is significant improvement in compressive strength and carbonation depth of mortar when the CO$_2$ pressure increases from 0.5 bar to 1 bar. However, little further improvement was observed when the pressure was increased from 1 bar to 5 bar, although there was a small but steady increase in the CO$_2$ uptake. Thus, 1 bar pressure could be considered as the threshold pressure.

• Increasing the CO$_2$ pressure from 0.5 bar to 5 bar does not significantly change the carbonation products in the highly carbonated layer (top 0-2 mm) of the paste sample.

8.1.2 Comparison of microwave heating with other methods for preconditioning cementitious materials

• A 30% higher compressive strength and 38% higher CO$_2$ uptake, and higher carbonation depth were observed for the MP mortar sample than that for the WP mortar sample. This is likely due to the much higher amount of water loss from the MP preconditioning process that facilitates the transport of CO$_2$, giving higher carbonation efficiency.

• With similar water losses from the AP and MP mortar samples, the MP process saves 95% preconditioning time of the AP process. In addition, a lower carbonation depth was found in the AP mortar sample. This is likely due to the lower porosity of the AP sample and over-drying of the top surface.

• The carbonation products were similar for all samples, irrespective of the differences in preconditioning methods. In addition, the CO$_2$ uptake and percentages of the different carbonate phases of CaCO$_3$ were similar in
the highly carbonated layer of the preconditioned samples after carbonation.

- Clusters of CaCO$_3$ were found in the AP sample (high degree of hydration) after carbonation, whereas for the MP, WP and NP samples (low degree of hydration) a more homogeneous distribution of CaCO$_3$ was observed after carbonation.

### 8.1.3 Effects of microwave-based preconditioning on properties of carbonated PC blends

- In comparison to a pure cement mortar, the threshold microwave-based preconditioning time was prolonged with the additions of GGBS and fly ash but remained the same with the addition of limestone.
- Compared with the pure cement mortar, the compressive strengths of mortars decreased, but the CO$_2$ uptake and carbonation depths increased with the three types of additions after preconditioning and 2h carbonation.
- The main carbonation products remained the same when different additions were added to the paste, with calcite the predominant phase present. However, aragonite was not found in the mortar containing limestone powder.
- After microwave-based preconditioning, the limestone powder mortar sample subjected to preconditioning and carbonation curing was the only composite showing higher strength at 28d, the fly ash mortar sample with carbonation exhibited lower strengths, while equivalent strengths was found in the GGBS mortar.
- In all samples with or without additions, little further hydration was found in the highly carbonated layers in the long term. In contrast, hydration continues in the semi-carbonated and uncarbonated layers.
- The paste sample containing limestone powder without carbonation produces the highest amount of C-S-H gel at 4h, but produces the least amount of C-S-H gel at 28d due to the mostly inert limestone powder.
The samples containing GGBS are more sensitive to carbonation curing when compared with the samples containing fly ash, which may be attributed to the coating of the CaCO$_3$ on the GGBS particles.

### 8.2 Future work

- **Determination of the water distribution in the cementitious materials under microwave heating**

  The water loss from microwave-based preconditioning is crucial as it determines the subsequent carbonation curing. However, the water is not lost homogeneously from all depths of the sample as water can only be lost from the top surface of samples. As a result, the water content is different for different depths of the sample after preconditioning. In this research, only the total water lost from samples was measured. The loss at different depths should be determined to have a better understanding of the conditions of samples prior to carbonation.

- **Future study of the ‘pumping effect’ due to the expansion of air voids entrapped in cementitious materials**

  The ‘pumping effect’ in literature refers to the phenomenon that the moisture becomes vapour when the internal temperature exceeds the boiling point, then the vapour generates extra pressure that accelerates the moisture migration. In our project, this phenomenon would not occur because the internal temperature is controlled at 70°C. However, a similar ‘pumping effect’ can happen due to the expansion of air voids entrapped in cementitious materials at mixing stage. The preliminary study also shows that with air voids added to the mortar samples, the mortar samples would crack due to the expansion of air voids, with visible paths for the migration of air voids. This effect is crucial as it is one of the main reasons that microwave heating gives a high rate of drying and homogeneous water distribution. However, there is no direct evidence regarding the ‘pumping effect’ in this study that facilitates the migration of water from the inside to the surface, and should be studied in further work.
Further study of the microwave non-thermal effect on cement hydration

The literature review briefly introduces the microwave non-thermal effect which reduces the activation energy of the sintering and chemical reaction. However, there is little study of the microwave non-thermal effect on the cement hydration. In this project, with similar temperature history, a higher degree of cement hydration is observed in samples subjected to microwave heating than conventional heating. This confirms the microwave non-thermal effect that accelerates hydration. However, this needs to be proved by more experiments in the future work.

Determination of the maximum temperature in the microwave-based preconditioning process

Increased temperature leads to improved preconditioning efficiency. The maximum temperature for microwave heating has been set at 70°C in this research and controlled by adjusting the power as it is supposed that heating above this temperature might cause the decomposition of ettringite leading to delayed ettringite formation later. However, even though the ettringite does decompose at higher temperatures, after carbonation, the calcium from the ettringite will precipitate as CaCO₃ decomposing the ettringite so it can no longer reform at a later age. Therefore, it is possible that the limit for 70°C may not be applicable for this combined regime and a higher maximum temperature can be applied.

Application of the permeable moulds in the microwave-based preconditioning process prior to carbonation curing.

In the demoulding process, the samples can be unavoidably damaged because the compressive strength at that time is still low. If the current moulds were replaced with permeable moulds, CO₂ could enter into the moulds without the need to demould the samples before carbonation, reducing any damage in the
demoulding process. In addition, the water vapour could escape during microwaving through the moulds to increase the water evaporation, thus facilitating subsequent carbonation curing. This would lead to a more homogeneous sample.

- **Investigation of the size effect on the microwave-based preconditioning and carbonation curing regime**

  In this study, only 50 mm cube mortar samples were studied. Size will affect both the water loss in the preconditioning process and the strength development in the carbonation process. The combined techniques should be applied to mortar and concrete with larger dimensions in order to satisfy industrial applications.
Reference


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