

IN-SITU PRODUCTION OF CALCIUM CARBONATE NANOPARTICLES
IN FRESH CONCRETE USING
PRE-CARBONATION
METHOD

by

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ABSTRACT

To reduce the carbon footprint of ordinary Portland cement (OPC)-based concrete, a novel technique, pre-carbonation process, has been developed to produce CaCO_3 nanoparticles in fresh concrete. In this technique, gaseous CO_2 is first absorbed into a slurry of calcium-rich minerals which is then blended with other ingredients to produce mortar/concrete. The objective of this work is to obtain an in-depth understanding of the underlying scientific mechanisms associated with the enhancement of strength and durability of the concrete induced by the new method. A comprehensive research plan has been carried out to study the carbonated slaked lime slurry and the effect of carbonated slaked lime slurry on the performance of OPC-based concrete, and to evaluate the potentials of the pre-carbonation method.

Experimental studies show that carbonating the calcium-rich mineral slurry with CO_2 can produce CaCO_3 nanoparticles and $\text{Ca}(\text{HCO}_3)_2$ in the slurry, and these carbonation products were dictated by four parameters of the pre-carbonation method: the duration and temperature of the carbonation, the concentration of the calcium source slurry, and the stirring method of the calcium source slurry during the carbonation. The mechanical properties and durability of the mortar/concrete made with the carbonated slurry were significantly improved, which can be attributed to major mechanisms induced by the pre-carbonation method: promoted hydration of the cement and denser microstructure of the mortar/concrete. Calorimetry testing showed that the hydration of OPC was greatly improved by the pre-carbonation because of the extra heterogenous nucleation sites provided by the CaCO_3 nanoparticles. XRD and TGA results revealed that more ettringite was produced in the mortar/concrete with pre-carbonated slaked

lime slurry. The overall volume of the hydration products of the cement was increased by the pre-carbonation, leading to denser microstructure of the mortar/concrete.

It has been found that the pre-carbonation can be used to the OPC-supplementary cementitious materials (SCMs) blended cement mortar/concrete, as evidenced by the improved mechanical properties achieved by these mortars produced by using the pre-carbonation method. A preliminary study was also conducted to examine whether other calcium-rich minerals, such as Class C fly ash and limestone, can be used as calcium source in the pre-carbonation method.

DEDICATION

This dissertation is dedicated to my parents. Thanks for your love, support, and encouragement through my study.

LIST OF ABBREVIATIONS AND SYMBOLS

Symbols

Al_2O_3	Aluminium oxide
CaCO_3	Calcium carbonate
CaCl_2	Calcium chloride
$\text{Ca}(\text{HCO}_3)_2$	Calcium bicarbonate
$\text{Ca}(\text{OH})_2$	Calcium hydroxide
CO_2	Carbon dioxide
CO_3	Carbonate
C_3A	Tricalcium aluminate (cement chemistry notation)
C_3S	Tricalcium silicate (cement chemistry notation)
d	Primary particle size
Fe_2O_3	Ferric oxide
Na_2CO_3	Sodium carbonate
ρ_g	Density of the particles
s_g	Surface area
SO_3	Sulfur trioxide
TiO_2	Titanium dioxide
w/c	Water-to-cement ratio
w/cm	Water to cementitious materials ratio
ZnO_2	Zinc peroxide

Abbreviations

ACC	Amorphous calcium carbonate
AFm	Alumina, ferric oxide, mono-sulfate
AFt	Alumina, ferric oxide, tri-sulfate
BET	Brunauer-Emmett-Teller
C-S-H	Calcium silicate hydrate (cement chemistry notation)
CH	Calcium hydroxide (cement chemistry notation)
CNTs	Carbon nanotubes
DTG	Derivative mass loss
EG	Ethylene glycol
GGFBS	Ground granulated blast-furnace slag
OPC	Ordinary Portland cement
Pre-C	Pre-carbonation
SCM	Supplementary cementitious material
SL	Slaked lime
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
TEA	Triethanolamine
UV	Ultraviolet
XRF	X-ray fluorescence
XRD	X-ray diffraction

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Many thanks to my dear friends and colleagues William Guin, Wei Pan, Shahrooz Amidi, Fengjuan Liu, Brandon Pritchett, and Yi Fang for their enormous help and support. Finally, I would also like to express my sincere gratitude to my parents, Zhiyun Qian and Juxiang Xiang, and my girlfriend, Yuqing Guo, for their encouragement and love throughout these years.

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CHAPTER 1

INTRODUCTION

1.1 Background

Ordinary Portland Cement (OPC)-based concrete is the most widely used construction material. The global use of concrete is only second to water, accounting for 70% of all building and construction materials [1]. Although OPC has many advantages such as easy of application, availability of the raw materials all over the world, the production of OPC releases large amount of green-house gases. One ton of cement clinker releases 0.98 tons of equivalent carbon dioxide, and cement industry accounts for 5% of global carbon dioxide emission [2,3]. At the same time, cement production is still growing by 2.5% annually and is expected to rise from 4.1 billion tons in 2015 to around 4.8 billion tons in 2030 [4]. To combat global climate change, the carbon footprint of OPC-based concrete should be reduced. To this end, two approaches have been proposed:

- 1) Reduce the amount of OPC used in concrete since OPC is the major contributor to the carbon footprint of concrete. This can be realized through partially replacing OPC with minerals or totally replacing OPC with alternative non-OPC binders which have lower carbon footprint [5–11]. Minerals commonly used to partially replace OPC can be classified as either reactive or nonreactive minerals. Reactive minerals can hydrate and/or react with hydration products of OPC and thereby enhance the long-term properties of concrete. They are commonly known as supplementary cementitious materials (SCMs).

- 2) Enhance the performance of concrete so that less OPC is needed in concrete or longer service-life of concrete can be reached. Among many technologies proposed to enhance the performance of concrete, the use of nanomaterials has received particular attention in last two decades [12,13].

1.2 Nanoparticles in OPC-based Concrete

Many nanoparticles, like nano-SiO₂, nano-TiO₂, nano-CaCO₃, nano-Al₂O₃ and even carbon nanotubes (CNTs) have been used in concrete [14–18]. When added into concrete, these nanomaterials can enhance the performance of concrete.

1.2.1 Working Mechanisms

The improvement on the performance of OPC-based concrete achieved by adding nanoparticles can be attributed to a few mechanisms:

- 1) Providing nucleation seeding sites for hydration products to promote the hydration of OPC [19,20]. Compared to other constituents in concrete, nanoparticles have a much higher surface area to volume ratio (Figure 1.1 [21]), which can serve as nucleation site for cement hydration.
- 2) Filling the pores in concrete to produce dense concrete with less binder [21]: Because the average particle size of calcium silicate hydrate (C-S-H) gel is about 10 nm, the addition of nanoparticles can fill the voids of produced concrete and hence optimize the packing density [22]. This effect is largely depended on the particle size and dispersion of nanoparticles in cement [22]. He and Shi reported 1% nanoparticles by weight of cement can effectively decrease the chloride ion permeability [23].
- 3) Reacting with hydration products to produce more solid binding phases [24,25]: Certain nanoparticles, like nano-SiO₂, can react with Ca(OH)₂ and produce C-S-H. This reaction

product can also serve as nucleation site to further promote the hydration of OPC.

Bjornstrom et al. revealed that colloidal silica can accelerate the phase dissolution of C_3S and the phase formation of C-S-H [19].

- 4) Reinforcing the interfacial transition zone of the concrete [26]. Nanoparticles can improve the structures of the interfacial transition zone between the cement paste and aggregates and thereby result in a more durable and stronger concrete [26].

In addition, new functions such as self-sensing [27,28] and self-cleaning [29,30] capabilities can be introduced into concrete by nanoparticles.

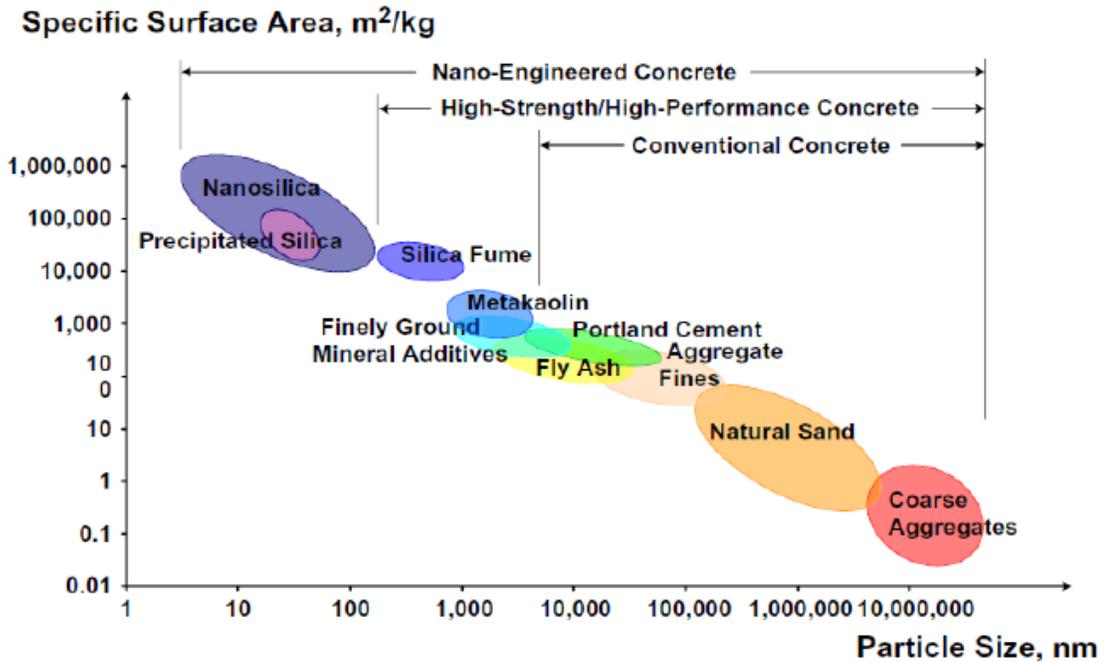


Figure 1.1. Particle size and specific surface area related to concrete materials [21]

1.2.2 Applications of Nanoparticles to Improve OPC-based Concrete

Among many nanoparticles mentioned above, SiO_2 nanoparticles are most often used in concrete. This is because in addition to the seeding and filling effects, nano- SiO_2 can react with $Ca(OH)_2$ in concrete to produce more C-S-H gel in concrete, which can significantly improve the

performance of concrete. Depend on the amount of nano-SiO₂ added (1%-5%), an increase of approximately 17–45% and 3–18% in compressive strength was observed at the 3rd and 28th d, respectively [31]. Calcium leaching is a big concern of the durability of concrete, and the addition of nano-SiO₂ can effectively reduce this phenomenon [32]. Some researchers also applied nano-SiO₂ on concretes with SCMs, especially fly ash, which reduces the early age strength development of the concrete. This negative effect of fly ash can be compensated by adding nano-SiO₂ which promotes the crystal growth of calcium hydrates [20]. However, due to consumption of Ca(OH)₂, the later age hydration of cement with fly ash is hindered [33].

There is also plentiful research on incorporation of nano-TiO₂ in concrete. Similar to nano-SiO₂, nano-TiO₂ can also improve the compressive and flexural strengths of the concrete [30,34]. TiO₂ is commonly used as photocatalyst which can convert toxic air pollutants to less toxic materials under ultra-violet (UV) light. Extensive studies have shown that cement mortars added with nano-TiO₂ also exhibit photocatalytic properties [29,30]. Experimental study shows that the more improvement on abrasion resistance of concrete can be achieved by adding nano-TiO₂ than adding the same amount of nano-SiO₂ [35]. The major adverse effect of adding nano-TiO₂ in concrete is that the shrinkage is induced by the addition of TiO₂, which can be controlled by careful dosage and particle size distribution [36].

Carbon nanotubes are graphitic sheets seamlessly rolled into tubular structures, with diameters ranging from nanometer to tens of nanometers, and lengths up to centimeters. CNTs have extraordinary mechanical properties, such as strength (tensile strength > 100 GPa), stiffness (Young's modulus of ~ 1.5 TPa), flexibility (20%-30% at failure) [37]. All these features, together with high aspect ratios and excellent thermal and electrical properties, make CNTs ideal candidate to reinforce and toughen concrete.

Extensive studies have been carried out to use CNTs to reinforce OPC [38–48]. Shah et al. [39] shows that CNTs can strongly reinforce the Portland cement matrix at the nanoscale once good dispersion of CNTs is obtained.

Once CNTs are added into the composite, dispersed CNTs are able to form a conductive percolating network in the matrix making the composite electrically conductive. Experimental studies have shown that this electrical resistance of CNT reinforced composites varies in proportion with the stress/strain, suggesting that CNT reinforced composites can sense their own straining [49,50]. Thostenson and Chou [51,52] also demonstrated that CNT nanocomposites can sense the damage in the composite. This is because damage in the composite, which usually starting from a micro-crack in the matrix, can break the conducting pathways in the percolating of the CNT network. As a result, a significant change of electrical resistance can be observed after the damage occurs. This self-sensing of strain/damage ability of CNT nanocomposites is of great importance to the health monitoring of structures.

Other nanoparticles such as nano-Fe₂O₃, nano-ZnO₂, nano-Al₂O₃, nano-CaCO₃, and nanoclay particles have also been added into OPC-based concrete. Experimental studies show that all these nanoparticles have the potential to improve the mechanical properties of cement composites [16,53–56], as summarized in Table 1.1. For example, Liu et al study shows that 1% of nano-CaCO₃ addition can improve compressive and flexural strength of cement paste greatly without influencing the consistency of cement [16]. This improvement can be attributed to the mentioned mechanisms associated with the addition of nanoparticles, as well as some other mechanisms pertained to CaCO₃, which will be discussed in detail in section 1.3.

Table 1.1. Improvement of strength of cementitious composites with nanoparticles at 28 d.

Types of nanoparticles	Concentration ¹	Compressive Strength improvement	Flexural Strength improvement	References
Nano-SiO ₂	3%	18.5%	6.7%	Wang [31]
Nano-TiO ₂	3%	12.8%	3%	Li [55]
Nano-Fe ₂ O ₃	3%	22.7%	26%	Li [55]
Nano-ZnO ₂	2%	2.2%	14.3%	Nazari [53]
Nano-Al ₂ O ₃	1.5%	15%	18.8%	Nazari [17,54]
Nanoclay	8%	7%	49%	Morsy [56]
Carbon nanotubes	0.005%	NA	25%	Konsta-Gdoutos [57]
Nano-CaCO ₃	1%	8%	8.3%	Liu [16]

Note: 1. The concentration is % in weight of the OPC.

1.2.3 Challenges of Applying Nanoparticles in Concrete

Although great potentials of nanomaterials have been confirmed by extensive studies, their real applications in concrete are very limited because of a few obstacles. The biggest obstacle is the low-cost efficiency of using nanoparticles. The cost of nanoparticles itself is still 100 to 1000 times higher than the OPC or other conventional raw-materials employed for OPC-based concrete [58]. This is because the production of nanomaterials requires relatively expansive chemical and physical process. For instance, the production of nanoparticles through mechanical attrition require high energy consumption [59]. The most widely used sol-gel method also involves very costly raw materials [60]. For this reason, the production of significant amount of OPC-based concrete is cost prohibitive [13] even with very low addition of nanoparticles.

Another major obstacle is the difficulty of dispersing nanoparticles in concrete. Due to strong van der Waals forces, nanoparticles conglomerate easily, making it difficult to uniformly disperse nanoparticles in concrete. A few techniques, such as the use of surfactants, ultrasonic

energy, and chemical functionalization can be used to disperse nanoparticles in concrete, but they may require extra equipment and cost, making it difficult to implement on larger scale. In addition, potential risks and health hazards of nanoparticles is also a concern which has not been sufficiently addressed [12].

1.3 CaCO₃ in OPC-based Concrete

Ground limestone (mainly consisting of calcite (CaCO₃)), with typical particle sizes comparable to cement, has traditionally been used as a filler to partially replace the fine aggregate [61] in OPC-based concrete. Water retention and workability of concrete can be improved by the addition of limestone powders. This is also the primary reason for the use of limestone powder in self-compacting concrete mixes [1].

Two methods are commonly used to introduce limestone into the OPC-based concrete. In the first method, limestone is added into un-ground OPC clinker and then co-ground with the clinker into fine powders, which is referred to as Portland limestone cements [62]. This cement is usually ground to a finer size to increase the rate of hydration and strength development of the concrete. This is necessary because of the dilution effect of the limestone powders, which can reduce the strength development rate of the concrete, especially at early stages of hydration [63]. In this cement, the limestone powder is usually smaller than cement particles because limestone is softer than the OPC clinker [64]. In the second method, ground limestone powders are directly blended with the ground OPC clinker.

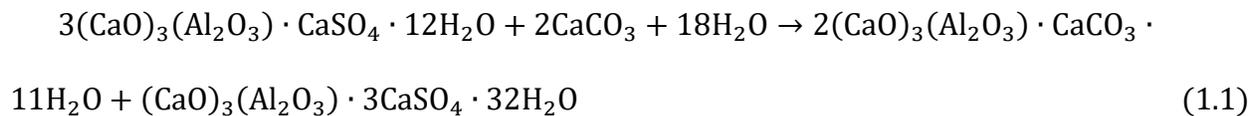
1.3.1 Working Mechanisms of Using Limestone Powder in OPC-based Concrete

Extensive studies in last decade show that ground limestone can also be used to partially replace OPC [65–67]. For example, ASTM C150 [68] specifies that up to 5% OPC can be replaced by limestone powder; While ASTM C595 [69] allows to use limestone powders to

replace up to 15% of OPC by for blended cements. This is because limestone powders can not only provide nucleating sites for hydration of OPC, but also have limited reactivity with the aluminate phases of OPC [70–72].

After very fine limestone powders added into concrete, they provide additional surface for the nucleation and growth of the hydration products of OPC. As a result, the hydration of OPC can be accelerated [70], and this acceleration is in proportion to the surface area of the limestone powders. Therefore, recent studies focused on using ultra-fine limestone particles (diameter less than 1 μm) into concrete to produce high performance concrete [8]. These very fine particles can provide much more nucleating sites than the coarse ones. In addition, the ultra-fine limestone powders can fill the voids of produced concrete and hence optimize the packing density [8].

Limestone powders also influence the distribution of lime, alumina and sulfate in the concrete and thereby alters the mineralogy of the hydrated cement pastes. Bessy first reported CaCO_3 could react with tricalcium aluminate (C_3A) to produce monocarbonate, which is more stable than monosulfate (AFm), as shown in Equation 1.1 [73]:



Because of excessive C_3A , ettringite can react with C_3A to produce AFm. With presence of carbonate, AFm will slowly dissolve and react with calcite to produce monocarbonate, which is more stable due to its much lower solubility [74]. This reaction is slower than the formation of ettringite [75]. The addition of calcite has no effect on C-S-H unless in regions where slight dilution can happen with existence of excessive calcite [72].

The final reaction products between calcite and OPC are mainly determined by the molar ratio of $\text{CO}_2/\text{Al}_2\text{O}_3$ and $\text{C}_3\text{A}/\text{SO}_3$, as shown in Figure 1.2 [72]. It shows that addition of calcite

can produce more ettringite, and more AFm is replaced by hemicarbonate. Formation of ettringite produces more solid products and reduces the porosity of the hydrated concrete due to the large volume expansion of the ettringite, and thereby increases the strength of the concrete. This can be seen from thermodynamic simulation shown in Figure 1.2, in which the total volume of minerals increases with the formation of ettringite induced by the addition of calcite until a maximum is reached at a $\text{CO}_2/\text{Al}_2\text{O}_3$ ratio of approximately 0.33. When more CO_3 is added, the monocarbonate is produced instead of hemicarbonate. Current study shows monocarbonate has a bulk modulus of 54 GPa [76], which is stronger than any other hydration product of cement. By introducing hemicarbonate and monocarbonate, it also can suppress or delay the conversion of ettringite to AFm [77]. Monocarbonate itself, however, is an unstable compound in sulfate and chloride environment and it will not help increase the sulfate resistance.

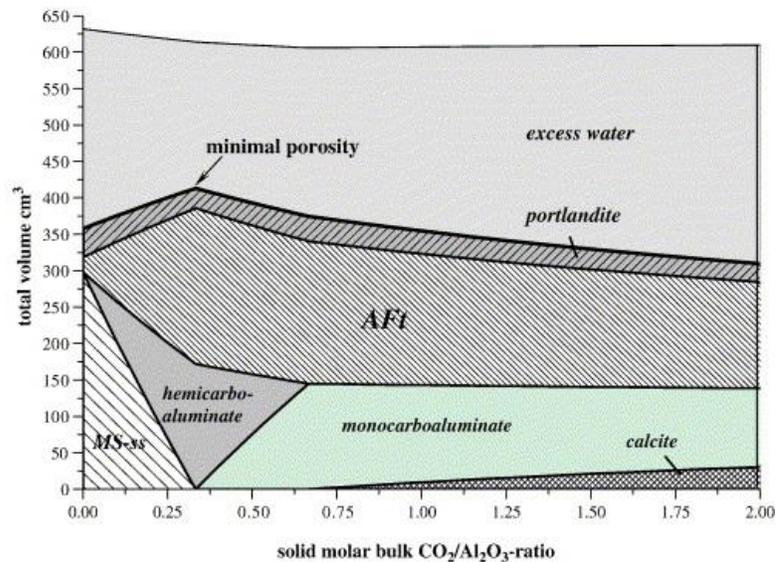


Figure 1.2. Volume changes of hydrate phases of a hydrated model mixture consisting of C_3A , portlandite and with fixed sulfate ratio ($\text{SO}_3/\text{Al}_2\text{O}_3 = 1$) in dependence of changing carbonate ratios ($\text{CO}_3/\text{Al}_2\text{O}_3$) at 25 °C [72].

1.3.2 Effect of Addition of Limestone on the Properties of Fresh Concrete

1.3.2.1 Heat Evolution

Although limestone is mostly considered as inert filler in fresh concrete, it still can influence the heat evolution because of additional surface provided for nucleation and growth of hydration products. Lothenbach et al. found the cement hydration was slightly increased with 4% limestone [70]. P´era et al. even reported more heat is generated in cement with 50% limestone than pure cement by isothermal calorimetry [78]. Based on a recent study, with fine limestone filler, there is a huge reduction in adiabatic temperature rise on an even strength basis [79]. The authors also claim that same strength with lower hydration heat can be achieved by the concrete using fine limestone filler [79].

1.3.2.2 Workability and Setting

As mentioned before, limestone was used to make self-compacting concrete due to its benefit on workability of concrete. Sprung and Siebel found that the workability of concrete is largely influenced by the particle size distribution of aggregates [80]. Later, Wang et al. found a wide particle distribution was beneficial to increase the packing density and reduce the water demand [81]. The cement with limestone addition has wider particle size distribution, suggesting a lower uniformity factor of Rosin-Rammler distribution in comparison with pure OPC. Tsivilis et al. reported that the mix with limestone cement had a better workability even with higher fineness [82]. Camiletti et al. also found limestone even helped to improve the workability of ultra-high performance concrete (UHPC) [8]. Greater flowability was achieved by adding more micro size calcium carbonate [8].

Setting results from the formation of a dense suspension of dispersed particles in an irreversible network of connected cement particles, which can resist shear force [83]. The fresh concrete can reach final setting with less than 5% C_3S hydrated by Vicat needle testing [83]. For controlling setting time, the sulfate ions have more impact than carbonate ions. Current studies

show setting time varies with the amount and size of the added limestone particles. Kato et al. found the setting time would be reduced with 10% limestone powder replacement [84]. This acceleration of hydration can be caused by high surface area of limestone powders surpassing the influence of their dilution effect. However, with more limestone replacement, both initial and final setting time were reduced. With same amount replacement of limestone powders, shorter setting time is achieved by using smaller particles [66]. There is a possible mechanism that more fine limestone increases the number of contact points between hydration products and raises the packing density of the microstructure, reducing the inter-particle spacing, thus leading to faster setting time [85]. The limestone addition also reduces the bleeding capacity of fresh concrete because the limestone particles can block capillary pores to obstruct the water movement in fresh concrete [86].

1.3.3 Effect of Limestone on Hardened Concrete

Current studies show there are several properties of hardened concrete can be improved with addition of limestone fines: mechanical properties, volume stability and durability.

1.3.3.1 Mechanical Properties

Most studies have shown that concrete can be stronger after adding finer limestone powder [8,65,67]. Nehdi and Mindess [67] reported that 10% limestone micro-fines replacement of OPC improves the strength of mortars at early ages. Limestone fine, however, has very limited reactivity in OPC-based concrete. Its acceleration effect diminishes with higher percentage replacement of OPC. Nehdi and Mindess [67] shows that significant strength loss occurs when more than 15% limestone fines is used. Micro limestone has been also reported to be effective to improve the mechanic properties of ultra-high performance concrete through enhancing particle packing density [65].

Nano-CaCO₃ particles have also been tested in concrete. Liu et al. [16] investigated the effect of nano-CaCO₃ particles (14-45 nm) on the performance of cement paste. It was found that the optimal amount of nano-CaCO₃ is 1%. Both the compressive and the flexural strengths of the cement paste can be improved without increasing the water requirement.

1.3.3.2 Volume Stability

The shrinkage of hardened concrete, due to the loss of capillary water, generates tensile stress, which can lead to cracks in hardened concrete. One of most common ways to reduce the shrinkage of concrete is to replace the cement with other cementitious materials or to reduce the cement paste volume in concrete. Current studies show that limestone fines can be added into concrete as inert filler so that the cement paste volume in concrete is reduced, leading to lower drying shrinkage of produced concrete. Kwan et al. reported the ultimate shrinkage strain is reduced by 28% with 8% limestone fines. The strength is also significantly increased [87].

However, the chemical shrinkage, which is the result of hydration reaction, is increased with presence of limestone fines due to its accelerating effect on cement hydration. Bouasker et al. reported that the chemical shrinkage is higher for cement containing limestone fines in first 24 h [88]. The monocarbonate, which is the reaction product between AFm and calcite, can also influence the chemical shrinkage because its density is higher than AFm. Kato found that chemical shrinkage decreased with more limestone powder in the early stage, but kept increasing for long time [84]. This is probably due to the inert filler effect of the limestone fines.

1.3.3.3 Durability

Low permeability is the key to achieve high durability in porous concrete structure. Current studies show that the permeability of concrete can be reduced by adding limestone filler due to better size distribution of the blended cement and reduction in the connectivity of the pores

[89,90]. Tsivilis reported limestone addition has a beneficial effect on the water permeability and the sorptivity of concrete, even with higher gas permeability compared to control samples [90]. Chen also observed similar results that limestone addition can substantially reduce the permeability of produced concrete by filling into the pores in concrete [89].

Concrete with limestone can be damaged by the formation of thaumasite because the presence of carbonate could favor the formation of this compound in cold and wet environment [91]. Thaumasite can be produced from the reaction between ettringite, C-S-H, and carbonate ions in the presence of water. The silicon derives from C-S-H and form thaumasite, which leads to decomposition C-S-H. The replacement of C-S-H by thaumasite results in the softening of the cement paste matrix into a white, mushy incoherent mass [92]. The carbonate ions can come from aggregates, cement filler, and even atmospheric carbonation [93]. According to the analysis of Irassar, thaumasite sulfate attack on concrete with limestone addition is mainly governed by the transport properties of mixture and the previous damage caused by expansive ettringite formation [94]. There is not enough evidence to show that the existence of limestone worsens the sulfate resistance. From field and laboratory studies, Hobbs found that the magnitude of thaumasite attack is determined by the following combination of conditions: a low temperature (less than 5 °C), wet conditions, exposure to sulfates associated with the magnesium cation, the prior formation of conventional sulfate attack products, and the presence of at least between 15% and 35% of calcium carbonate by mass of the cement [95]. Therefore, a low portion of limestone addition (<10%) has almost no impact on the thaumasite attack resistance of the concrete.

1.3.4 Current Methods to Produce Micro/Nano Calcium Carbonate

Grinding is the most common process to produce micro size CaCO_3 because of its mass production ability. Stirred ball mills have been used in recent years to grind particles to sub-

micron sizes due to their easier operation, simpler construction, higher grinding rate, and lower energy consumption compared to other fine-grinding machines [96]. In order to prevent particle aggregation, grinding aids, such as triethanolamine (TEA), ethylene glycol (EG), and poly-acrylic acid, are commonly used to improve the efficiency of the grinding process [97,98].

Nano-CaCO₃ particles can be synthesized through either solution method or carbonation method [99]. The solution method mainly uses double decomposition reaction, such as CaCl₂ and Na₂CO₃. The morphology and particles size of produced CaCO₃ particles can be controlled by the addition of different kinds of additives [99]. The carbonation method uses CO₂ gas as carbonate source to directly carbonate Ca(OH)₂ slurry. This is the most used industrial process because of its convenience and high productivity.

1.3.5 Summary

Limestone powder has been used in concrete for last two decades. Many benefits as summarized in Table 1.2 have been achieved by adding limestone fines in concrete due to higher surface area, enhanced packing density induced by limestone fines, and limited reactivity of the CaCO₃ in OPC-based concrete.

Table 1.2. Summary of CaCO₃ benefits and concerns

Benefits	Concerns
<ul style="list-style-type: none"> • Enhanced compressive and flexural strengths • Reduction in permeability and bleeding capacity • Improved durability • Increased workability • Reduced water usage 	<ul style="list-style-type: none"> • Limited percentage use due to thaumasite attack • Strength reduction with large volume replacement

Although many benefits can be achieved by using limestone fines, their use in concrete is limited to low replacement levels. At higher replacement levels (more than 10-15% of OPC), most of the limestone is non-reactive, and the strength of concrete is reduced due to the dilution effect of the limestone powder.

1.4 Innovation: Pre-carbonation

In this study, we propose to in-situ produce calcium carbonate nanoparticles in fresh concrete through a pre-carbonation process. Here calcium carbonate nanoparticles are chosen because they not only have been proven effective in enhancing the performance of concrete as summarized in Section 1.3, but also can be produced at very low cost through CO₂ bubbling method. Since nanoparticles are in-situ produced, any costs associated with packing, storage, shipping, and dispersing are eliminated. This aqueous production strategy also avoids direct dealing with dry nano powder, thus minimizes the exposure of humans to nanomaterials and the related health hazard. Therefore, the new method proposed in this study has the potential to enable real implementation of nanoparticles in concrete. The pre-carbonation method is a simple two-step mixing approach to in-situ produce CaCO₃ nanoparticles in fresh concrete. As shown in Figure 1.3, in step I, calcium-rich mineral is added into the mixing water to form diluted calcium-rich slurry. Then CO₂ is bubbled into this slurry to carbonate the calcium-rich mineral into CaCO₃ and Ca(HCO₃)₂. Many cementitious materials used in the concrete – such as OPC and some SCMs, such as high calcium fly ash, blast furnace slag, and cement kiln dust – can be used here as calcium-rich minerals. For practical application, a large-scale method used by Kachinski [100] to carbonate cement kiln dust can be used to carbonate the slurry. Many methods [101–103] used to carbonate minerals to permanently store CO₂ in carbonate minerals

can also be used. The carbonated mixing water is then mixed with other ingredients of concrete in the second step to produce concrete samples, as shown in the step II in Figure 1.3.

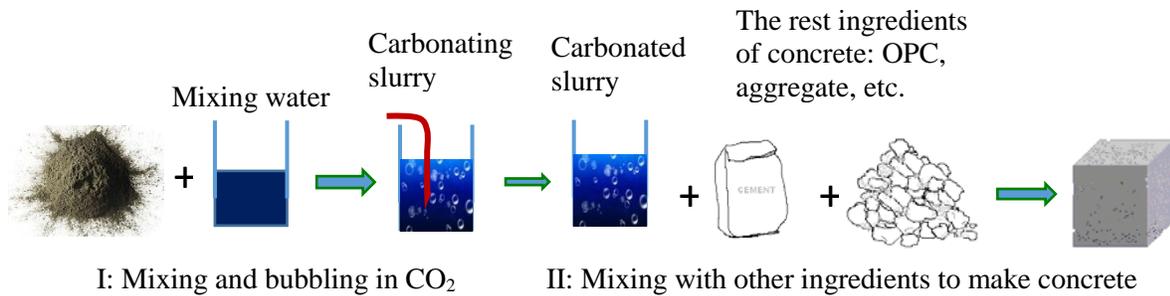


Figure 1.3. Manufacturing concrete through the pre-carbonation method.

1.5 Research Significance

The proposed approach has many advantages in enhancing the sustainability of concrete:

- 1) It significantly enhances the strength and durability of the produced concrete due to several mechanisms activated by the pre-carbonation method. Structures constructed by this concrete either consume less OPC or have longer service-life, leading to a more sustainable infrastructure system.
- 2) Pre-carbonation enjoys many advantages over using limestone powder in concrete. Nanoparticles can be produced in-situ in the pre-carbonation method. The cost of grinding and dispersing of limestone nanoparticles is eliminated.
- 3) It promotes more effective applications of mineral fillers in concrete to replace OPC, especially for non-reactive mineral fillers. Currently, non-reactive mineral fillers used to replace OPC consist mainly of limestone powder due to its synergistic effects with OPC and SCMs. Pre-carbonation possesses all of these synergistic effects. Therefore, other non-reactive mineral fillers such as quartz powder can be used together with the pre-carbonation technique to achieve the same or even better results as limestone powder. Utilization of more mineral fillers in construction materials creates many environmental benefits, such as

conserving landfill space, reducing the depletion of natural resources, reducing energy consumption, and reducing CO₂ emissions.

- 4) Pre-carbonation makes beneficial use of CO₂ and thereby reduces the carbon footprint of concrete. Although pure CO₂ is used in this study, it can be envisioned that flue gas can be directly used as the source of CO₂ to reduce the cost. In this way, the new method can be used to capture CO₂, too.

1.6 Research Objectives

With an ultimate goal to develop the pre-carbonation method into a practical green technology to enhance the sustainability of concrete, we have developed the following specific objectives for this study:

- (i) to obtain an in-depth understanding of the underlying scientific mechanisms associated with the significant enhancement of strength and durability of concrete induced by the new method;
- (ii) to establish the general guidelines for applications of this technology, and evaluate the potential of this technology on enhancing the mechanical performance and durability of concrete;
- (iii) to apply the proposed technology to design and synthesize new green binder.

To reach these objectives, a comprehensive research plan has been carried out and presented in this dissertation as summarized in Section 1.7.

1.7 Structure of Dissertation

This dissertation consists of six chapters:

- Chapter 1 introduces a general introduction of the background, motivation, innovation, and objectives of this research project.

- Chapter 2 focuses on the characterization of calcium carbonate particles produced by pre-carbonation method under various conditions, including the duration, temperature, of pre-carbonation, slaked lime concentration and dispersion method.
- Chapter 3 evaluates the effects of pre-carbonation techniques on the early age hydration and long-term properties of OPC-based mix. Results from strength tests, permeability and pore structure tests, isothermal calorimetry, drying shrinkage, setting time, isothermal calorimetry, drying shrinkage, and microscopy are presented.
- Chapter 4 explores the application potential of pre-carbonation technique on the blended cement with fly ash or metakaolin. Results from XRD, TGA, isothermal calorimetry, strength, and durability tests are presented and discussed.
- Chapter 5 presents some additional studies related to other calcium-rich minerals. In previous chapters, slaked lime was using to absorb CO_2 to produce CaCO_3 . In this chapter, other calcium-rich minerals like fly ash was investigated as calcium source in pre-carbonation method.
- Chapter 6 draws conclusions of this work and points out work needed to be done in the future. A general guideline for cementitious materials with pre-carbonation technique is also discussed in this chapter.

CHAPTER 2

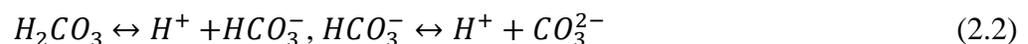
CARBONATING SLAKED LIME SLURRY

2.1 Introduction

This chapter focuses on the first step of the pre-carbonation method: carbonating the slaked lime slurry through bubbling CO₂. The purpose of this step is to produce a carbonated slurry, which consists of CaCO₃ nanoparticles, Ca(HCO₃)₂, and residual Ca(OH)₂. The composition of these chemicals and the size of the produced nanoparticles are major features affecting the properties of the produced mortar/concrete. These features of the carbonated slurry are determined by the major carbonating parameters, including the duration and temperature of the carbonation, slaked lime concentration, and dispersion method of the slurry. Therefore, the objective of this chapter is to correlate the major carbonating parameters to the properties of the carbonated slurry through a series of experimental study. The morphology and size of the produced CaCO₃ were investigated by X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The surface area of the produced particles was measured using Brunauer–Emmett–Teller (BET) method.

2.2 Carbonation Process

To carbonate slaked lime slurry, CO₂ gas is first dissolved in water forming carbonic acid (Equation 2.1). Then carbonic acid dissociates to H⁺ and CO₃²⁻ (Equation 2.2).

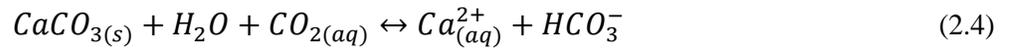


As shown in Equation 2.3, with the help of H⁺ ions, Ca²⁺ ions in the calcium-rich minerals are released, which react with CO₃²⁻ to form calcium carbonate precipitates. These particles usually are particles in nanometers.



According to Ostwald's step rule [104], the least stable polymorph will precipitate first, which is amorphous calcium carbonate (ACC) with particle size less than 50 nm[105]. Zeta potential of this newly formed CaCO₃ was measured as -10 mV [106]. Zeta potential is known for determining the stability of colloidal, and the particle can only be stable with Zeta potential higher than +30 mV or lower than -30 mV. Therefore, the produced ACC particles tend to aggregate to eventually form micro-sized particles [107]. This unstable ACC is transformed into one or more of its three polymorphs in the following order: ACC to vaterite, aragonite, and calcite, and this phase transforming process can be affected by several factors, such as temperature, additive, pressure, dispersion method, and chemical environment [108–113].

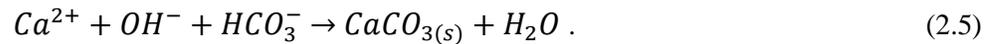
If more CO₂ is bubbled into the slurry, some of calcium carbonate will dissolve to produce Ca(HCO₃)₂, which has much higher solubility in water, as shown in Equation 2.4.



A few key parameters, such as the duration and temperature of carbonation, the concentration of the slaked lime slurry, and the method used to stir the slurry, all play important roles on the composition of the produced carbonated slurry, and therefore, were systematically examined in this chapter.

1. Temperature: The temperature at which carbonation is carried out to determine the carbonation rate of the slaked lime and the phase transformation of the produced CaCO₃ nanoparticles. Calcite phase is formed through vaterite intermediate at low temperature

(<30 °C). While the aragonite phase is produced at high temperature (≥40 °C) [112]. In this study, two different temperatures were used to carbonate the slurry: 7 °C and the ambient temperature of 23 °C. The first temperature is chosen because at this temperature, the formation of amorphous calcium carbonate will be more stable, leading to a smaller particle size. In addition, at this temperature, CO₂ has a higher solubility in water, and therefore, more Ca(HCO₃)₂ can be produced in the carbonated slurry. At ambient temperature and pressure, the maximum concentration of CO₂ in water is 0.0339 mol/L, which can produce a saturated Ca(HCO₃)₂ solution at 0.00827 mol/L. At 7 °C, the concentration of saturated Ca(HCO₃)₂ solution can be enhanced to 0.0102 mol/L. Ca(HCO₃)₂ can react with Ca(OH)₂ from cement to produce more CaCO₃, as shown in Equation 2.5. On one hand, the produced CaCO₃ nanoparticles can provide extra seeding sites for the hydration of cement. On the other hand, this reaction consumes Ca²⁺ in fresh concrete, which may delay the formation of hydration products.



2. Concentration: The concentration of the slaked lime slurry is another important factor affecting the result of the carbonation. Longer carbonation duration is needed for higher concentration of the slurry, which will produce larger size of the produced CaCO₃ particles due to higher chance of particle aggregation.
3. Dispersion method: Due to high surface energy, the aggregation of precipitates is inevitable [106]. It is important to limit this aggregation process so that higher surface area of the produced CaCO₃ particles can be achieved. To this end, slaked lime slurry is stirred during the carbonation by two methods: Ultrasonication and magnetically stirring.

2.3 Materials and Methods

2.3.1 Materials

Pure carbon dioxide gas with a purity of 100% was used as carbonate source. Slaked lime, used as calcium source, was manufactured by the Montevallo Plant (owned by Lhoist North America). Figure 2.1 shows the XRD pattern of slaked lime as received. The pattern was obtained with Bruker D8 Discover at a scanning rate of $10^\circ/2\theta$ per minute using Cu $K\alpha$ radiation at 35 kV and 20 mA. A small amount of CaCO_3 was found in slaked lime, which was possibly resulted from the carbonation of the slaked lime in air. Two concentrations were used to make slaked lime slurry in this study: 0.14 mol/L (1% by weight of water) and 0.52 mol/L (3% by weight of water). The water used in this study was deionized water.

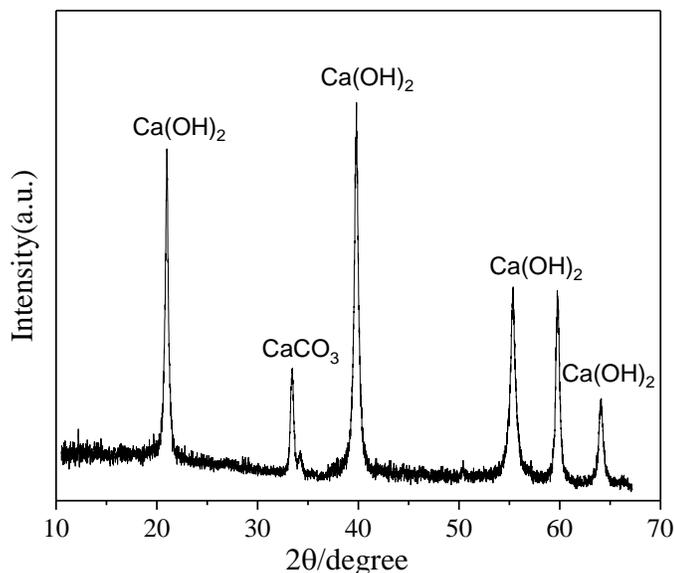


Figure 2.1. XRD pattern of the slaked lime as received

2.3.2 Experimental Setup

After mixing slaked lime and water for 3 min in the glass container, CO_2 was bubbled into the slaked lime slurry, as shown in the Figure 2.2. Air stone was used to help disperse CO_2 gas homogenously in the slurry. Depending on the dispersion method used, a magnet stir or an

ultrasonic bath was placed below the container. The stirring rate was 800 rpm for the magnet stir. The delivery gas pressure was fixed at 6 psi during carbonation. A pH meter was used to monitor the carbonation degree.

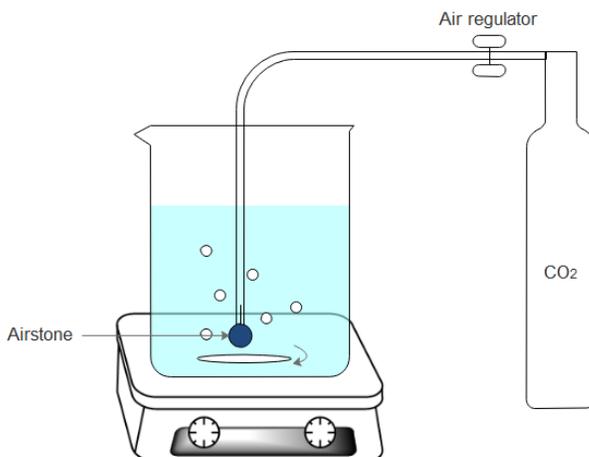


Figure 2.2. Schematic illustration of carbonation method

2.3.3 Characterization Methods

2.3.3.1 pH Value

The degree of carbonation of the slaked lime can be monitored through measuring pH value of slaked lime slurry using a pH meter. The initial temperatures of the water for this study were chosen as 7 °C and 23 °C, and the slaked lime concentrations were chosen as 1% and 3% by the weight of water. 500 mL slaked lime slurry was carbonated using the setup shown in Figure 2.2.

2.3.3.2 Microscopy

A JEOL 7000 FE SEM was used to examine the precipitated particles of pre-carbonation method with accelerating voltage from 20 kV to 30 kV. Two concentrations of slaked lime, 1% and 3%, were used so that the effect of the concentration of slaked lime on the morphology of the precipitates can be evaluated. Two carbonation temperatures, 7 °C and 23 °C, were used to examine the effect of carbonation temperature on the morphology of precipitates. The

carbonation duration for 1% and 3% slaked lime slurry were 10 min and 15 min, respectively. The precipitates were gathered using a 20 nm filter paper with vacuum suction. Ethanol was used to wash the precipitates to prevent further aggregation and phase transformation during filtration. The filtration process took 15 min for 1% carbonated slaked lime slurry and 30 min for 3% carbonated slaked lime slurry due to the small size of the filter paper. The precipitated was then dried in the oven at 60 °C for 24 h. The dried powder samples were coated with gold to minimize the charging before placed into the sample chamber of SEM.

2.3.3.3 XRD with GADDS

XRD is powerful to determine crystal structure of a crystal. All XRD analysis was performed with Bruker D8 Discover at a scanning rate of $10^\circ 2\theta$ per minute using Cu $K\alpha$ radiation at 35 kV and 20 mA. The samples were prepared in the same way as the one used to prepare samples for SEM examination. The XRD patterns were obtained by scanning at $15-80^\circ 2\theta$.

2.3.3.4 Surface Area

CaCO_3 precipitates can serve as heterogenous nucleation sites in cement hydration. It is necessary to measure the surface area of the precipitates produced by the carbonation method. This was done by using AutoChem II from Micromeritics Instrument Corporation based on BET theory. The precipitates were prepared in the same way as described in SEM analysis.

2.4 Results and Discussion

2.4.1 pH Value and Degree of Carbonation

The pH value of the slaked lime slurry during carbonation was continuously monitored, and results are shown in Figure 2.3. $\text{Ca}(\text{OH})_2$ is slightly soluble in water. Its solubility in water decreases with increasing temperature. At ambient temperature (23 °C), 0.173 g $\text{Ca}(\text{OH})_2$ can dissolve in 100 mL water. Therefore, both 1% and 3% slaked lime slurries should produce

saturated $\text{Ca}(\text{OH})_2$ solution. The initial pH value of the slurries was measured between 12.4 and 13.1, as shown in Figure 2.3. The initial pH value of the 3% slurry is slightly higher than that of the 1% slurry. This is probably due to the small amount of impurities, such as Na_2O and Al_2O_3 , in the slaked lime. With more CO_2 bubbled into the slurry, produced CO_3^{2-} reacted with Ca^{2+} to form CaCO_3 precipitates, leading to a slow reduction of the pH value of the slurry, as shown in Figure 2.3. After all slaked lime was consumed, further carbonation caused a sudden drop of the pH value of slurry. Continued bubbling CO_2 gas into the slurry converted some CaCO_3 into $\text{Ca}(\text{HCO}_3)_2$, as shown in Equation 2.4. During this stage, the pH value of the slurry reduced slowly with the carbonation. Eventually, the pH value stopped at about 5.9, suggesting that no more CO_2 can be absorbed and reaction shown in Equation 2.4 also stopped. This ultimate pH value of the carbonated slurry is determined by the solubility of CO_2 in water. Figure 2.3 also shows that much longer time is needed to carbonate the 3% slaked lime slurry than the 1% one.

Since the reaction between the carbonic acid and $\text{Ca}(\text{OH})_2$ is exothermic, the temperature of slurry was raised a little bit after carbonation. For the 1% slurry, the temperatures increased from the initial 7 °C and 23 °C by 4 °C and 1.8 °C, respectively, after 12 min carbonation. The temperatures of the 3% slurry were increased by 9 °C and 5 °C for the initial temperature 7 °C and 23 °C, respectively, after 20 min carbonation. This change in temperature could affect the maximum concentration of bicarbonate in the slurry because the solubility of $\text{Ca}(\text{HCO}_3)_2$ is dependent on the temperature.

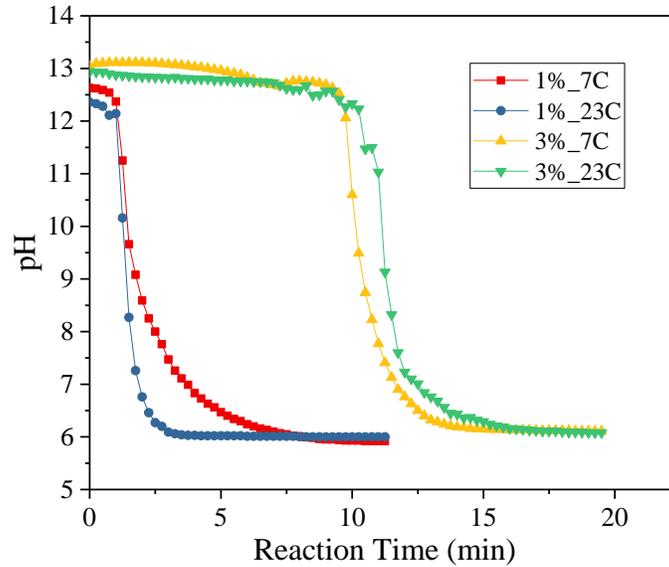


Figure 2.3. Change in the pH of the slaked lime slurry with respect to temperature of carbonation and concentration of slaked lime

2.4.2 Microscopy

Figure 2.4 shows the precipitates which is an intermediate form between ACC and calcite, produced by carbonating the slaked lime slurry at 7 °C for 10 min. These particles have an average diameter 20 nm. It can be seen clearly that the precipitates were agglomerated to form large particles.

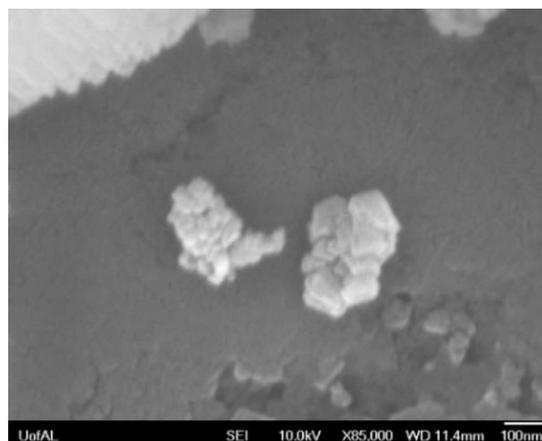
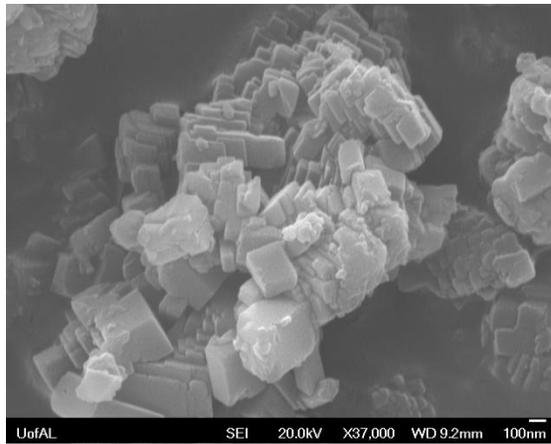
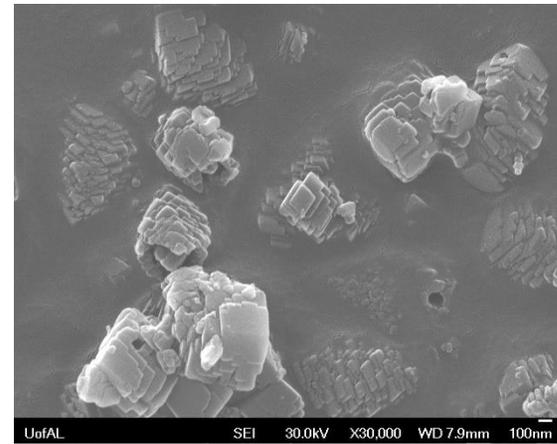


Figure 2.4. SEM image of calcium carbonate produced by carbonating the slaked lime slurry

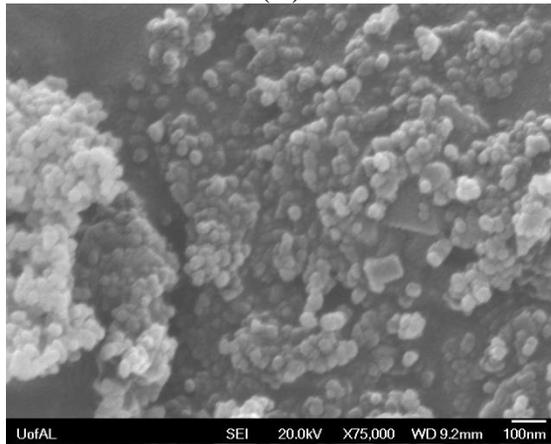
The morphology of the produced CaCO_3 was greatly influenced by the concentration of the slaked lime and the carbonation temperature, as revealed by Figure 2.5 (a-d). For 1% slaked lime, the precipitates tended to be plate-like and stacked together. This morphology was also reported by Wen et al. with carbonation method [114]. This plate-like CaCO_3 particles will eventually become cubic-like calcite in the slurry. Large CaCO_3 particles can be produced at higher carbonation temperature. Figures 2.5 (a) and (b) shows that the CaCO_3 particle produced at 23 °C has a diameter of 180 nm, which is about 1.5 times larger than that produced at 7 °C. This trend was even more evident in 3% slaked lime slurry. Carbonating at 7 °C, the produced CaCO_3 particles with a spherical shape have an average diameter of 40 nm, as shown in Figure 2.5 (c). When the carbonation temperature was resized to 23 °C, the average diameter of the plate-like particles increased to 200 nm, as shown in Figure 2.5 (d.). It should be pointed out that all the precipitate samples were produced by allowing 24 h drying in the oven. The precipitate particles inevitably grew larger due to the aggregation in this process. As a result, the observed particle sizes shown in Figures 2.4 and 2.5 are larger than those in the carbonated slurry. In addition, small particles with size less than 20 nm in the slurry were not captured due to the size of the filter paper. No notable difference was found on the morphology of the precipitates produced by stirring using a magnet stir and ultrasonic bath. It means the transformation from ACC into a more stable polymorph is not influenced by the ways to stir the slaked lime slurry during carbonation process.



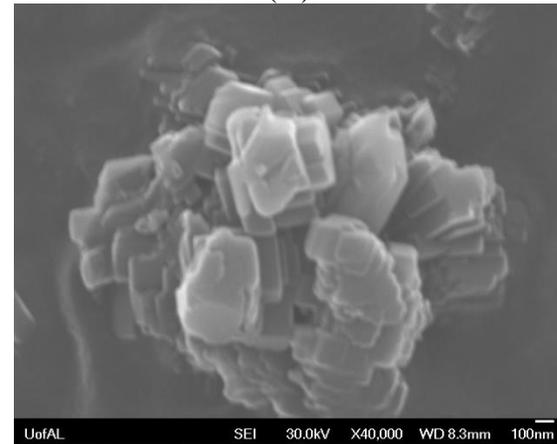
(a.)



(b.)



(c.)



(d.)

Figure 2.5. Comparison of calcium carbonate precipitates produced with carbonation method with different carbonation temperatures and slaked lime concentrations: (a.) 1% slaked lime at 7 °C, (b.) 1% slaked lime at 23 °C, (c.) 3% slaked lime at 7 °C, (d.) 3% slaked lime at 23 °C.

2.4.3 XRD

The XRD diffractograms of the calcium carbonate produced by the carbonating the slaked lime are shown in Figure 2.6. It can be seen that all CaCO_3 produced at different conditions are calcite, which is in agreement with the observation of SEM images. The change in slaked lime concentration and temperature of carbonation method made no influence on the crystallinity of precipitates. This is not surprising since the precipitate was dried in an oven for 24 h before the measurement. With such a long time in the open air, all unstable phases of CaCO_3 with presence of water should be able to transform into calcite.

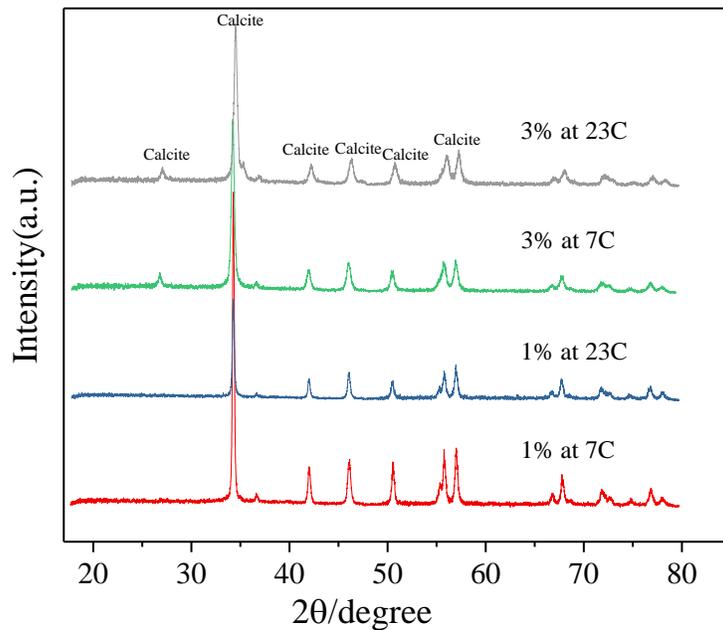


Figure 2.6. XRD patterns of calcium carbonate precipitates produced by carbonating the slaked lime slurries

2.4.4 Surface Area

The surface areas of the precipitates produced by the 1% slaked lime slurry carbonated for 10 min at 7 °C and 23 °C, were 16.69 m^2/g and 14.1 m^2/g , respectively. These results are more than 400 times higher than cement particles (average surface area is about 0.4 m^2/g). It should be pointed out the actual surface area of precipitates in the slurry produced by the carbonation

should be much higher. This is because the surface area was measured on the filtered precipitates which grew larger than those in the slurry after drying in the oven for 12 h. In addition, all those particles smaller than 20 nm (hole size of filter paper) in the solution, which have larger surface area than the large particles, were missed in the surface area measurement.

The size of primary particles of the precipitate can be estimated by Equation 2.6 by assuming the particles are granular [115],

$$d = 6/(s_g * \rho_g) \quad (2.6)$$

where, d is primary particle size, s_g is the surface area, and ρ_g is density of the particles (in this case 2.71 g/cm^3 for calcite). Calculation suggests that the primary particle sizes for 1% precipitates produced at 7°C and 23°C , are 130 nm and 157 nm, respectively. At lower carbonation temperature, the particle size of precipitates is smaller, as revealed by this calculation.

The surface areas of the 3% precipitates produced by carbonating at 7°C and 23°C were $6.5 \text{ m}^2/\text{g}$ and $4.1 \text{ m}^2/\text{g}$, respectively, which are smaller than anticipated. This can be attributed to the long filtration process. It took significantly longer time to filter the precipitates than that needed in the case of 1% slurry. As a result, more precipitates aggregated to form large particles, leading to much smaller surface area.

Stirring the slurry with an ultrasonic bath can slightly increase the surface area of precipitates. For example, the surface area of the precipitate produced by carbonating 1% slaked lime slurry at 7°C was increased to $17.8 \text{ m}^2/\text{g}$ by using the ultrasonic bath from $16.69 \text{ m}^2/\text{g}$ by using the magnetic stirrer.

2.5 Conclusions

This chapter examine the effects of the major carbonation parameters on the produced slurry. The following conclusions are drawn based on the experimental works carried out in this chapter.

1. The duration needed to fully carbonate the slaked lime slurry is proportional to the concentration of slaked lime in the slurry.
2. The concentration of slaked lime slurry affects the morphologies of the produced calcium carbonate. Larger calcium carbonate particles can be produced by using higher carbonation temperature.
3. The surface area of the precipitates produced by the carbonation method was more than 400 times higher than that of the cement particles. Higher surface area was achieved by carbonating a lower concentration of the slaked lime slurry.
4. Slight improvement on the surface area of the produced precipitates by stirring the slurry using an ultrasonic bath than a magnetic stirrer. The dispersion methods appear to have negligible impact on shapes of the produced CaCO_3 .

CHAPTER 3

EFFECT OF PRE-CARBONATION ON THE PERFORMANCE OF OPC-BASED CONCRETE

3.1 Introduction

The effects of adding limestone powders on the performance of OPC-based concrete and the associated working mechanisms were reviewed in Chapter 1. In Chapter 2, the precipitates produced from carbonating the slaked lime slurry were studied. In this chapter, the effect of the carbonated slaked lime slurry on the performances of OPC-based mortar is examined. Properties of both the fresh and hardened concrete are studied. Four carbonation factors were also experimentally investigated in this chapter to help understand the mechanisms of pre-carbonation method.

3.2 Materials and Methods

3.2.1 Materials

The type I/II cement produced by Sakrete Inc. was used in this research. Its chemical composition obtained from X-ray fluorescence (XRF) analysis is presented in Table 3.1. From Bogue calculation based on ASTM C150 [68], this cement has 53% C_3S , 25.7% C_2S , 8.6% C_3A , and 7.8% C_4AF . Slaked lime was manufactured by Montevallo Plant (owned by Lhoist North America). The fine aggregates are river sand with bulk specific gravity of 2.70 and water absorption capacity of 0.95%. The coarse aggregates are crushed limestone with dry specific gravity of 2.74 and water absorption capacity of 0.7%. All aggregates were oven-dried for 12 h

at 110 °C and cooled down for 12 h before mixed with other ingredients. The ground limestone powder, which contains 94% CaCO₃, was manufactured by Dudadiesel.

Table 3.1. Chemical composition of cement

Oxide Composition	Cement (%)
SiO ₂	22.94
TiO ₂	0.21
Al ₂ O ₃	4.89
Fe ₂ O ₃	2.57
MnO	0.03
MgO	3.52
CaO	64.85
Na ₂ O	0.20
K ₂ O	0.81
LOI	2.52

3.2.2 Mix Proportions

Six groups of mortar samples were made to evaluate the effects of the proposed pre-carbonation method in compressive strength of the mortar, as shown in Table 3.2. As shown in this table, the control group is the cement mortar with water to cement (w/c) ratio of 0.5 produced without using the pre-carbonation method. Limestone group is obtained by adding 1% of slaked lime by weight of the mixing water to the control one. Similarly, the Limestone group was produced by adding extra limestone powders to the control group. The amount of limestone was equal to the amount of calcium carbonate precipitated can be produced by carbonating 1% slaked slurry. The remaining three groups were produced by the proposed pre-carbonation method. As shown in the table, group 1% was produced by pre-carbonating the slaked lime slurry with a concentration of slaked lime as 1% of the mixing water. Similarly, groups 3% and 5% refer to the groups produced by pre-carbonating 3% and 5% slaked lime, respectively. These

three groups were used to determine the effect of the amount of pre-carbonated slaked lime on the performance of the mortar. To estimate the effectiveness of pre-carbonation on mortar with different w/c ratios, another six groups of mortar samples were made, as shown in Table 3.3. In this table, control and the pre-carbonated mortar samples were made with three w/c ratios (0.3, 0.4, 0.6). Two groups of concrete (one control and one pre-carbonated group) were produced to estimate the effect of the pre-carbonation on the elastic modulus of concrete, as shown in Table 3.4. It should be mentioned that the addition of slaked lime/limestone replaced same amount of cement to avoid confusion caused by the additional binder.

Table 3.2. Mix proportions for cement mortars produced with/without pre-carbonation method (lbs/yd³)

Constituent	Control	SL	Limestone	1%	3%	5%
Cement	607.0	604.0	604.0	604.0	597.9	591.8
Water	303.5	303.5	303.5	303.5	303.5	303.5
River Sand	1530.0	1530.0	1530.0	1530.0	1530.0	1530.0
Slaked Lime	-	3.0	-	3.0	9.1	15.2
Limestone	-	-	4.0	-	-	-
Pre-Carbonation	-	-	-	Yes	Yes	Yes

Table 3.3. Mix proportions for cement mortars with different w/c ratios (lbs/yd³)

Constituent	0.3		0.4		0.6	
Cement	1011.7	1008.7	758.8	755.8	505.8	502.8
Water	303.5	303.5	303.5	303.5	303.5	303.5
River Sand	1530.0	1530.0	1530.0	1530.0	1530.0	1530.0
Slaked Lime	0	3.0	0	3.0	0	3.0
Pre-Carbonation	-	Yes	-	Yes	-	Yes
Superplasticizer	4.8	4.8	-	3.0	-	-

Table 3.4. Mix proportions for cement concrete with/without using pre-carbonation method (lbs/yd³)

Constituent	Control	1%_Pre-C
Cement	610	606.8
Water	325	325
Crushed Limestone	1722	1722
River Sand	1419	1419
Slaked Lime	-	3.25
Pre-Carbonation	-	Yes

3.2.3 Characterization Methods

3.2.3.1 Setting Time

Vicat needle test was used to evaluate the effect of pre-carbonation on the initial and final setting time of cement paste according to ASTM C191 [116]. To achieve the normal consistency according to ASTM C187 [117], the w/c ratio for both the control and pre-carbonated pastes was chosen as 0.3. Pre-carbonated cement paste samples were produced by mixing cement with slaked lime slurries with concentrations varying from 1% to 5% pre-carbonated at 7 °C. The carbonation time for 1%, 3%, and 5% were 10 min, 15 min, and 25 min, respectively. The setting time of a group of cement paste samples made with OPC and un-carbonated slaked lime was also measured.

3.2.3.2 Isothermal Calorimetry

Isothermal calorimetry test based on ASTM C1679 and ASTM C1702 [118,119] was carried out to examine the effect of pre-carbonation on the hydration of the cement paste with w/c ratio of 0.5. The rate of heat release and total heat released by hydration of the cement pastes can be directly measured. I-Cal 2000HPC and I-Cal 4000HPC from Calmetrix Incorporation were employed in this test.

The cement paste samples were made by first dissolving specified slaked lime into 500 g deionized water, and stirring for 3 min. Three concentrations of slaked lime, 1%, 3%, and 5%, were used so that the effect of the amount of slaked lime on the hydration of the cement paste can be evaluated. The mixed slurry was then carbonated through bubbling CO₂ for certain time. Both the control and the pre-carbonated specimens were made at the same initial mixing temperature. The control cement paste specimen was produced by adding 50 g cement to 25 g deionized water and mixing for 2 min before placed into the calorimeter. The pre-carbonated cement paste samples were produced in the same way as the control group except that pre-carbonated slaked lime slurries were used to replace mixing water. The hydration heat produced in the first 30 min of the test was deleted to minimize the effect induced by mixing cement paste. Measurements were recorded up to 72 h.

3.2.3.3 XRD with GADDS

XRD was useful to study the effect of pre-carbonation on hydration products, such as CH and ettringite, in cement paste [120]. The content of minerals can also be measured. The XRD patterns of all cement paste samples were obtained by scanning between 6° -66°2θ with Bruker D8 Discover at a scanning rate of 10°2θ per minute using Cu Kα radiation at 35 kV and 20 mA on ground paste powders.

3.2.3.4 Thermogravimetric Analysis (TGA)

TGA was also used to identify hydration products of both the control and pre-carbonated cement paste samples by measuring the mass change associated with the thermal degradation. A quantitative analysis of different hydrated phases from TGA can be used to confirm the observation from XRD patterns. To this end, the paste samples prepared in the same way as those used in calorimetry test were ground with a ceramic mortar and dried in the air. Then its

weight was measured using a Simultaneous Thermal Analyzer 8000, which is purchased from PerkinElmer, from 30 °C to 1000 °C at 10 °C per minute. Cement paste samples were tested samples at two ages (4 and 8 d).

3.2.3.5 Microscopy

A JEOL 7000 FE Scanning Electron Microscopy (SEM) was used to examine the effect of pre-carbonation on the microstructure of the produced cement paste samples. The cement paste samples were prepared with the same proportion as those used in the calorimetry test. These paste specimens were cut into small cubic pieces by diamond blade saw and then finely polished with abrasive papers of 220, 320, 400, 600, 800, 1200 grit. Gold(Au) coating was then applied to minimize the charging.

3.2.3.6 Porosity and Density

Porosity of pre-carbonated cement paste was measured using helium intrusion porosimeter by Quantachrome Poremaster to evaluate the effect of pre-carbonation on the porosity of the produced cement paste. The w/cm ratio is 0.5 for all control and pre-carbonation group. The cylindrical paste specimens were prepared with a diameter of 24.6 mm and a height of 23.2 mm. After 7 d curing in a sealed plastic bag, these specimens were soaked in ethanol to stop the hydration of the cement for 3 d at ambient temperature. The average of the results of three duplicated samples is reported in this study. The bulk density of prepared pastes was also determined using the same equipment.

3.2.3.7 Strength and Modulus of Elasticity

3.2.3.7.1 Compressive Strength

Compressive strength of mortar samples was measured to estimate the potential of pre-carbonation on the strength development of the produced mortar. To this end, mortar samples

with six different mixes as shown in Table 3.2, were produced and tested. The first three mixes were used to make mortar samples without using pre-carbonation method. The rest mixes were used to produce pre-carbonated mortar samples with different pre-carbonating conditions, as described in detail later.

These mortars were cast into 50×100 mm cylinders according to ASTM C305 [121]. A vibration table was employed to consolidate the specimens. After stored in sealed plastic molds for 24 h, these specimens were demolded and cured in lime-saturated water at ambient temperature until the compression test was conducted. Before testing, all specimens were wiped with paper towel to remove water on the surface of specimens. The compressive strength of these specimens was measured at ages of 3, 7, and 28 d, respectively, using a Humboldt concrete compressor at a loading rate 35 ± 7 psi. The average values of three duplicated specimens were reported.

Pre-carbonating the slaked lime slurry involves four major parameters: the dose of slaked lime, the way to disperse the slaked lime particles, carbonation duration, and carbonation temperature. Their effects on the compressive strength of the produced mortar samples were studied through varying the pre-carbonating conditions as follows:

- The dose of slaked lime. Three doses of slaked lime were used as shown in Table 3.2. Our study suggests that to fully carbonate these slaked lime, the carbonation durations were chosen as 10 min, 20 min, and 25 min for 1%, 3%, and 5% slaked lime, respectively.
- Dispersion method: To produce more uniform dispersion of slaked lime and facilitate its carbonation, the slaked lime slurry was excited by an ultrasonic bath or stirred using a magnetic stir during the carbonation. Only 1% slaked lime was considered in this test.

- Carbonation duration: Three carbonation durations (10 min, 15 min, 20 min) were used to pre-carbonated 1% slaked lime slurry.
- Carbonation temperature: Two carbonation temperature (7 °C and 23 °C) were used to pre-carbonate the slurry.

It was also noticed the w/c ratio can affect the performance of pre-carbonation technique.

Therefore, three different water to cement ratios were used to manufacture concrete mortar samples, as shown in Table 3.3. All the samples were produced by pre-carbonating 1% slaked lime for 10 min Superplasticizer was added to group with 0.3 and 0.4 w/c ratio so that similar workability was achieved for both the control and the pre-carbonated groups.

3.2.3.7.2 Flexural Strength

Flexural strengths of mortar samples were measured to evaluate the effect of pre-carbonation on the flexural strength of cement mortars. Two different doses of slaked lime (1% and 3%) were used to make mortar samples, as shown in Table 3.2 according to ASTM C348 [122]. The fresh mortars were cast into 40 × 40 × 160 mm steel prism molds and compacted with a vibration table. The molds were sealed with plastic sheet for 24 h before demolding. All the specimens were then cured in a moist chamber until the testing age. Similar to the compressive tests, three duplicated specimens were measured at 7 d and 28 d with a MTS QTest/25. The average of these three specimens were reported.

3.2.3.7.3 Modulus of Elasticity

The moduli of elasticity were measured according to ASTM C469 [123] for the control and pre-carbonated concrete samples. The mix designs for both samples are shown in Table 3.4. The pre-carbonated samples were manufactured by pre-carbonating 1% slaked lime carbonated at 23 °C. Both the control and pre-carbonated samples were cast into 100 × 200 mm cylinders. The

axial deformation of the samples was measured by using an extensometer with 4 in gage length from Humboldt. The modulus of elasticity of the sample was measured at the ages of 7 d and 28 d and reported as the average of three duplicated specimens.

3.2.3.8 Durability Test

3.2.3.8.1 Water Absorption

Water absorption can be used as an indicator of the durability of the OPC-based concretes [124]. There is a strong linear relationship between the water absorption and the permeability of the concrete. Therefore, the objective of this study is to estimate the effect of pre-carbonation on the durability of the produced mortar through water absorption measurement. To this end, the rates of water absorption of both control and pre-carbonated mortars with mix proportion shown in Table 3.2, were obtained based on ASTM C1403 [125]. Three duplicated specimens with size of $50 \times 50 \times 50$ mm were cast and stored in a moist chamber covered by plastic sheet to prevent dripping water for 24 h before demolding. After that, all the specimens were demolded and cured in a sealed plastic bag at 23 °C. After 28 d, the specimens were dried in an oven at 110 °C for at least 24 h. When the difference between two successive measurements of the weight of the specimen were less than 0.2%, the specimens were taken out of the oven and cooled in the ambient environment. After measuring the width and length of the soaking surface and the initial weight, all the specimens were immersed 3 mm below water. The weight of three duplicated immersed mortars for each group was measured at 0.25, 1, 4, and 24 h. The surface water of specimens was wiped down with damp cloth before each weight measurement. The average of these samples was reported.

3.2.3.8.2 Sulfate Resistance Test

Sulfate resistance of the blended cements was tested on the mortar bars prepared based on ASTM C1012 with dimension of $1 \times 1 \times 11$ in. [126]. The w/c ratio of the mortar is 0.485, and the ratio between river sand and cement is 2.75 for all control and pre-carbonated specimens. After casting, the specimens were initially cured in a sealed container and placed into an oven at 35 ± 3 °C for 24 h. Then the specimens were demolded and cured in saturated lime water at 23 °C until an average compressive strength of 2850 psi measured by cubic specimens made in same batch was reached. After recording the initial length, all these mortar bars were submerged in the 50 g/L sodium sulfate solution which was produced by dissolving anhydrous sodium sulfate purchased from VWR with a purity of 99% into deionized water. The lengths of these cement mortars were measured using a comparator after 1, 2, 3, 4, and 8 weeks. The average of four duplicated samples of each group was reported.

3.2.3.9 Drying Shrinkage Test

Pre-carbonation may reduce the Ca/Si ratio of C-S-H since some calcium is consumed by CaCO_3 . It is known that lower Ca/Si ratio can result in higher shrinkage [127]. Therefore, drying shrinkage test was carried out to ensure that pre-carbonation doesn't increase the drying shrinkage of the produced concrete. To this end, $1 \times 1 \times 11$ in. prismatic cement mortar samples were manufactured using the mix proportion shown in Table 3.2 based on ASTM C 305 [121]. The measurement of drying shrinkage was in accordance with ASTM C 596 [128]. The specimens were demolded after 24 h and cured in saturated lime water. The specimens were taken out of the lime water at 72 h. Initial measurements were made with a digital comparator conforming the requirements of ASTM C490 [129]. Then these specimens were stored in an environmental chamber with a temperature 23 °C and a relative humidity of 50%. Drying

shrinkages were measured at 7, 14, 21, and 28 d for the mortar samples using a comparator. Four duplicated specimens were made and their average values are reported.

3.3.3.10 Pore Solution Test

Pre-carbonation may lower the pH value of the calcium-rich slurry which could interfere with OPC hydration or pose a risk of steel corrosion. To address this concern, the pH values of the pore solutions of both the control and pre-carbonated mortar samples with the mix proportions shown in Table 3.2 were measured. A set-up similar to the one developed by Barneyback and Diamond [130] was used to extract the pore solution from the cement mortar, as shown in Figure 3.1. About 250 g mortar sample at age of 7 d was smashed in a plastic bag with metal hammer and then placed into a testing chamber. A Humboldt 500k compression frame was then used to apply compressive forces up to 300 kips to the chamber. The extracted solution was diluted 100 times to ensure there is adequate solution to immerse the pH probe.



Figure 3.1. View of the device extracts the pore solution from cement mortar

3.3 Results and Discussion

3.3.1 Setting Time

Current studies show that adding nanoparticles can increase the hydration rate of cement because of small particle size and high surface areas of the nanoparticles, which can serve as nucleating seeds for the hydration products of OPC, leading to a shorter setting time [30].

Table 3.5 shows the setting time of cement paste produced with or without using the pre-carbonation method. The initial and final setting times for the control paste produced without using slaked lime are 135 and 201 min, respectively. If 1% uncarbonated slaked lime was added to this control group, the final setting time of the cement paste was reduced, as shown by the SL_1% group in Table 3.5. This can be attributed to binding function of slaked lime, which not only provide more CH in the cement paste, but also increase the pH value of the fresh paste, which can facilitate the dissolution of the OPC clinker in water. If this slaked lime was carbonated by bubbling CO₂, both the initial and final setting times were further reduced compared to control group, suggesting that pre-carbonating can accelerate the setting of the cement mortar. This is not surprising since pre-carbonation can precipitate the CaCO₃ nanoparticles in the water. With these additional nanoparticles, the mortar can set faster than without carbonation. Similarly, the initial and final setting time was reduced to 126 min and 179 min with 3% slaked lime, respectively. Compared to uncarbonated 3% slaked lime, pre-carbonated slaked lime further reduced the setting time caused by the acceleration of hydration of cement due to the nanoparticles and some uncarbonated slaked lime residue.

When the slaked lime content was increased to 5%, the setting times of the sample produced without using pre-carbonation method were further reduced due to the binding effect of the slaked lime. After this slurry was pre-carbonated, the produced mortar exhibits much longer

setting time, as shown by the sample of 5%_Pre-C group in Table 3.5. This may be caused by the reduction of pH value in the slurry induced by the pre-carbonation. With 5% slaked lime, the pH value of the mortar is very high, which can accelerate the dissolution of OPC clinker and, therefore, facilitate the hydration of OPC. After carbonation, the pH value of the mortar was reduced, leading to a relatively slower dissolving of the OPC clinker even with produced nanoparticles.

Table 3.5. Setting times of cement mortar produced with/without using pre-carbonation technique

Mix	Pre-carbonation	Setting times (min)	
		initial setting	final setting
control	NO	135	201
1%_SL	NO	143	196
1%_Pre-C	YES	126	185
3%_SL	NO	122	179
3%_Pre-C	YES	109	160
5%_SL	NO	80	150
5%_Pre-C	YES	105	174

3.3.2 Isothermal Calorimetry

3.3.2.1 Effect of Pre-carbonation on Hydration Heat

Calorimetry results of cement paste samples produced with and without using pre-carbonation method are shown in Figure 3.2. In this figure, the pre-carbonated sample was produced by carbonating 1% slaked lime slurry at 23 °C for 10 min stirred with a magnet stir. Except the initial region of high heat release (heat of dissolution) and dormant stage between 0.5 h and 5 h, pre-carbonation significantly improves the power of the hydration heat of the OPC, as shown in Figure 3.2. In this figure, two peaks which are induced by the hydration of tricalcium silicate (C₃S) and tricalcium aluminate (C₃A) can be identified for both the control and the pre-

carbonated samples. Both of them are significantly higher after pre-carbonation. This figure clearly suggests that the rate of hydration of OPC was promoted by the pre-carbonation, presumably due to the higher surface area induced by nanoparticles in-situ produced by the pre-carbonation method [12].

Figure 3.2 also shows that pre-carbonation actually slightly extends the dormant stage. This can be attributed to the reaction between the bicarbonate ions in the carbonated slurry with calcium ions in cement paste, to produce calcium carbonate nanoparticles. This reaction consumes the calcium ions in the fresh cement paste, delaying the formation of the hydration products such as C-S-H and CH in the paste. As a result, the dormant stage of the hydration was slightly increased. Figure 3.2 also shows that the accumulated released hydration heat per gram of cement at 72 h was improved up to 20% by the pre-carbonation method, clearly indicating that pre-carbonation can significantly promote the hydration of OPC at early age.

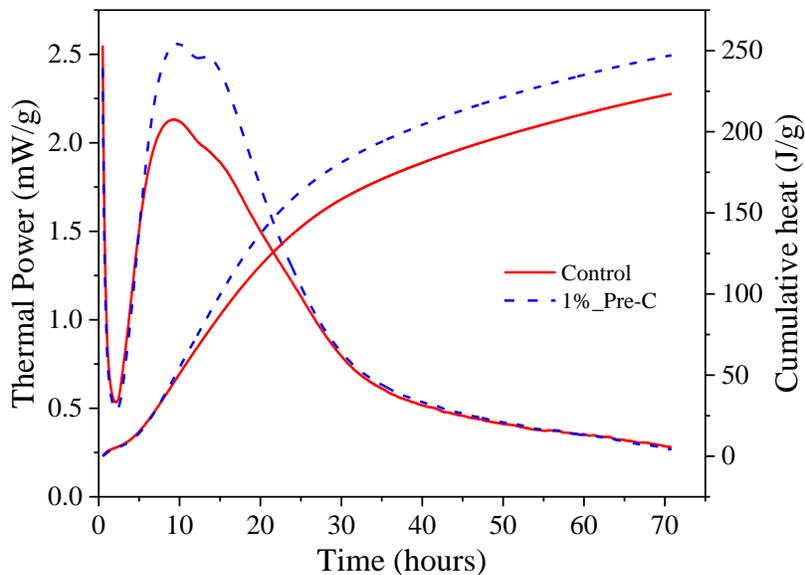


Figure 3.2. Effect of pre-carbonation on the hydration heat of cement paste.

The promoting effect of pre-carbonation at the early age can be attributed to the seeding effects of the calcium carbonate particles. As described before, calcium carbonate particles can

be produced either by the reaction between the slaked lime and CO_2 during the pre-carbonation or the reaction between the $\text{Ca}(\text{HCO}_3)_2$ in the pre-carbonated slaked lime and CH in cement paste during the mixing and the fresh cement paste. To distinguish the contributions to the promotion of hydration of these two types of calcium carbonate particles, a new cement paste sample was produced by only using $\text{Ca}(\text{HCO}_3)_2$ solution. In this way, only the nanoparticles produced by the reaction between the $\text{Ca}(\text{HCO}_3)_2$ and CH were present in the produced cement paste. The $\text{Ca}(\text{HCO}_3)_2$ solution was prepared by first carbonating the slaked lime slurry for 20 min at 23 °C, which was then sealed and settled for 24 h. After that, the top clear solution which is $\text{Ca}(\text{HCO}_3)_2$ solution was taken to mix with cement. The hydration heat released by the produced cement paste is presented in Figure 3.3.

Figure 3.3 shows that the thermal power of the hydration of the cement was slightly increased by using $\text{Ca}(\text{HCO}_3)_2$ solution. The total hydration heat released by one gram of cement with $\text{Ca}(\text{HCO}_3)_2$ solution is increased by only 4% compared to 20% in the case with precipitates. This slight promotion effect of the $\text{Ca}(\text{HCO}_3)_2$ solution should be attributed to the nanoparticles produced by the reaction between $\text{Ca}(\text{HCO}_3)_2$ and CH. Since the maximum concentration of CO_2 in water is 0.0339 mol/L at 23 °C, the concentration of saturated $\text{Ca}(\text{HCO}_3)_2$ solution is 0.00827 mol/L according to chemical equilibrium. With such low content of $\text{Ca}(\text{HCO}_3)_2$, the amount of CaCO_3 nanoparticles produced in the cement paste is very little, leading to very limited promotion of the hydration of the cement. Compared with Figure 3.2, it can be concluded that the CaCO_3 precipitate produced during the carbonating the slaked lime is the main reason responsible for the promoting effect of the pre-carbonation on the hydration of cement. Similar to Figure 3.2, due to the consumption of calcium and OH^- ions by the reaction between

$\text{Ca}(\text{HCO}_3)_2$ and CH, two peaks represents hydration of C_3S and C_3A slightly shift to right, indicating a slightly longer dormant stage.

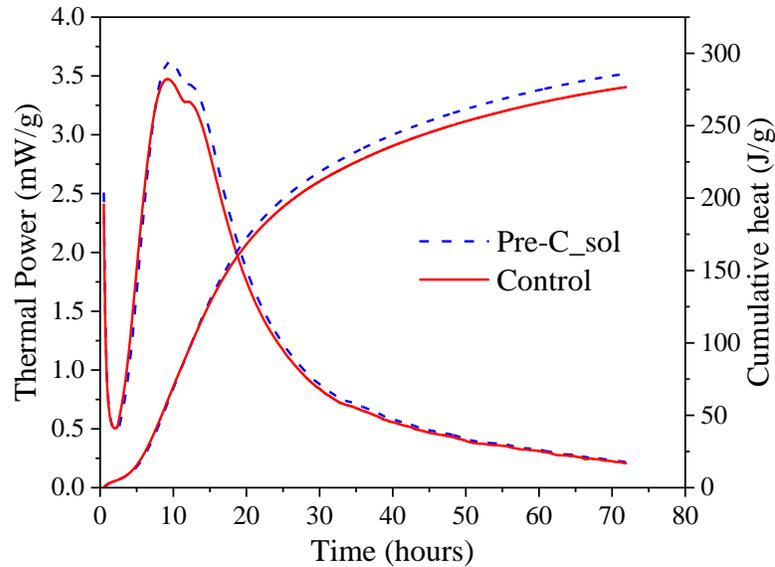


Figure 3.3. Isothermal calorimetry curves of cement pastes with/without $\text{Ca}(\text{HCO}_3)_2$ solution

Isothermal calorimetry tests were also carried out on two cement pastes. The first one was made by adding limestone powders with an average diameter around $10\ \mu\text{m}$. The amount of the limestone powders was chosen to be equal to the amount of calcium carbonate precipitated can be produced by carbonating 1% slaked slurry. The other one was made by adding 1% uncarbonated slaked lime. Testing results are shown in Figure 3.4. It can be seen that neither the limestone group nor the slaked lime group can have significant effect on the hydration of the cement pastes. The negligible promoting effect of ground limestone can be attributed to its size, which is much bigger than the nanoparticles produced in the pre-carbonation method. While the negligible effect of the slaked lime confirms the necessary of carbonating the slurry before mixing with the cement. Based on calorimetry tests shown in Figures 3.2 to 3.4, we can conclude that pre-carbonation can significantly improve the early age hydration of cement pastes. Although the major reason responsible for this promoting effect is the CaCO_3 nanoparticles

produced during the carbonating the slaked lime slurry, the promoting effect cannot be achieved by simply replacing the in-situ produced CaCO_3 particles with limestone powders or uncarbonated slaked lime.

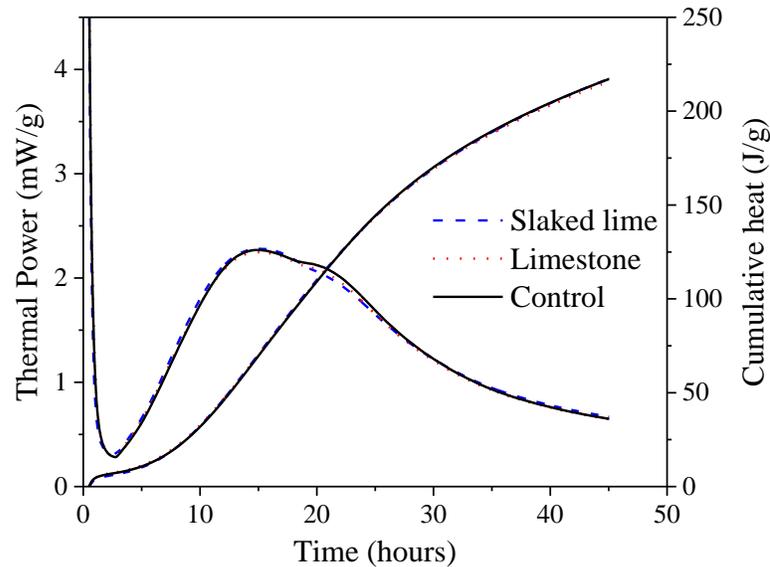


Figure 3.4. Isothermal calorimetry curves of cement pastes with limestone and slaked lime

3.3.2.2 Parameters Study with Isothermal Calorimetry

As mentioned in chapter 2, four major factors can affect the effect of pre-carbonation: dispersion method, concentration of the slaked lime, temperature of carbonation, and duration of carbonation. Isothermal Calorimetry tests were therefore carried out to examine the effects of these factors on the hydration of cement paste at the early age (up to 72 h).

3.3.2.2.1 Dispersion Method

To achieve better carbonation results of slaked lime, the slaked lime particles should be homogeneously dispersed into the mixing water during the carbonation. Although surfactants are usually used to disperse small particles in water, they cannot be used in pre-carbonation method due to their retarding effect on the hydration of cement. Therefore, two mechanical methods, stirring with a magnetic stir and sonicating with a ultrasonic bath, were used to disperse slaked

lime in the mixing water during the pre-carbonation. In the first method, slaked lime slurry was continuously stirred by a magnet stir during the carbonation. In the second method, the slaked lime particles were continuously sonicated through placing the slaked lime slurry into an ultrasonic bath during the carbonation. The produced pre-carbonated slurries were then used to make cement paste, and their calorimetry test results are shown in Figure 3.5. It can be seen that higher hydration rate of cement was achieved through pre-carbonating 1% slaked lime sonicated with ultrasonic bath. About 4% more accumulated hydration energy was achieved by sonicating the slurry than magnetically stirring it. In addition, the maximum thermal power of the first peak of the sonicated group comes 15 min earlier than the one of the magnetically stirred group, indicating that the former paste has a shorter dormant stage than the second one. The difference between the calorimetry results of these two pastes clearly suggests that better pre-carbonation result can be achieved by sonicating the slurry than stirring with a magnetic stir. This is because of the better dispersion of slaked lime particles and the produced CaCO_3 nanoparticles can be obtained by the sonication, as well established in numerous existing studies. Better dispersion of these particles leads to more extra surface area. As a result, more nucleating sites are available to the hydration of cement, which promotes the hydration of the cement.

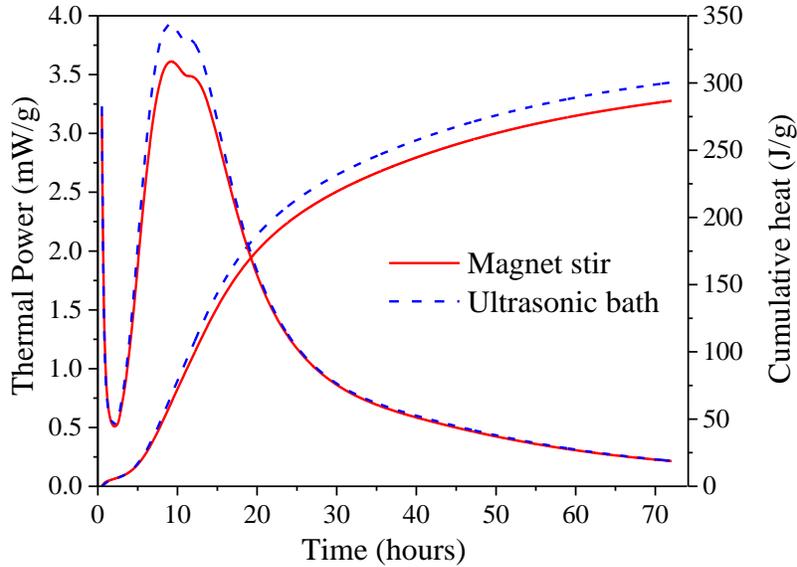


Figure 3.5. Isothermal calorimetry curves of cement pastes pre-carbonated with ultrasonic bath and magnet stir

3.3.2.2.2 Temperature of Carbonation

The temperature at which the pre-carbonation is carried out also plays an important role in the hydration of the cement paste. Two cement pastes were produced by using 1% slaked lime pre-carbonated for 10 min at 7 °C and 23 °C, respectively. The control groups for these two pastes were made with the same initial mixing temperature as the pre-carbonated ones. This was done by tuning the temperature of the mixing water used in the control group, which is the same as the temperature of the carbonated slurry. The curing temperature in the calorimeter chamber for 7 °C and 23 °C groups are 15 °C and 23 °C, respectively, which were the temperatures of the mix measured above.

Calorimetry test results of these pastes and their control groups are shown in Figure 3.6. It can be seen that higher thermal power peaks were achieved by pre-carbonating the slurry at ambient temperature (23 °C) than at a lower temperature (7 °C). This suggests that more nanoparticles can be produced by pre-carbonating the slurry at higher temperature. In addition, pre-carbonation at lower temperature (7 °C) can lead to longer dormant period, as shown in

Figure 3.6. This can be attributed to more $\text{Ca}(\text{HCO}_3)_2$ produced by carbonating the slaked lime slurry at the lower temperature because more CO_2 can be dissolved in water at lower temperature. Our calculation shows that the concentration of the produced $\text{Ca}(\text{HCO}_3)_2$ in the carbonated slurry can be increased by 23% if the carbonation temperature is decreased from 23 °C to 7 °C. With higher concentration of calcium bicarbonate, more OH^- and Ca^{2+} ions were consumed, leading to delayed formation of CH or C-S-H. Nevertheless, the accumulated energy released from the paste pre-carbonated at 7 °C surpassed the control group after 36 h, suggesting that short term retarding effect of the pre-carbonation at low temperature does not affect its promotion effects on the hydration of cement. This is possible because more hydration products were precipitated on the seeding sites provided by the CaCO_3 nanoparticles. As a result, less were precipitated on the cement clinker particles, leading to a thinner diffusion barrier on the surface of the clinker. In this way, the reaction between the clinker and water is facilitated.

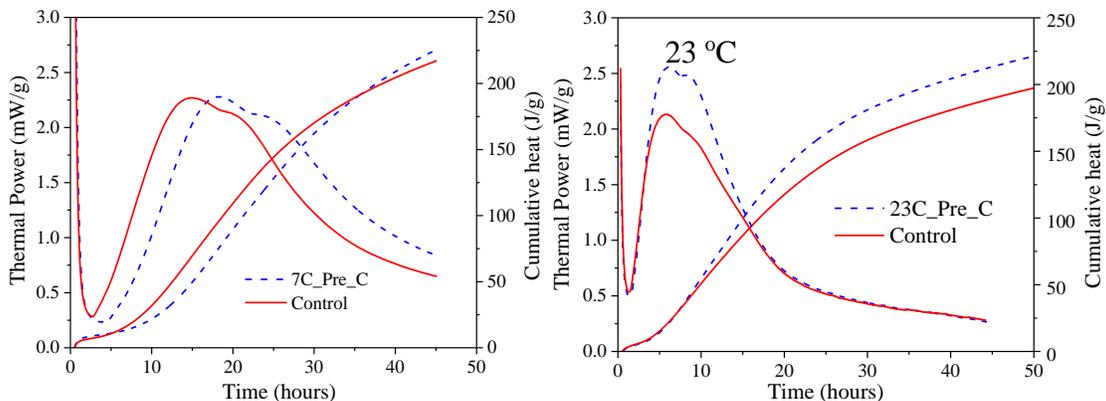


Figure 3.6. Isothermal calorimetry curves of cement pastes with slaked lime pre-carbonated at 7 °C and 23 °C

3.3.2.2.3 Duration of Carbonation and The Concentration of The Slaked Lime

Duration of the carbonation and the concentration of the slaked lime are another two important factors affecting the hydration of cement pastes produced by the pre-carbonation method. Calorimetry rests were therefore carried out on cement pastes produced with slaked

slime slurries at three concentrations (0.5%, 1%, and 3%) carbonated with three durations (10 min, 15 min, and 20 min) and results are shown in Figure 3.7. The carbonation temperature for all groups were 23 °C. It should be mentioned that different durations of carbonation can cause different initial temperature of the fresh cement paste due to the thermal energy released from neutralization reaction between the carbonic acid and the slaked lime. Therefore, the data obtained at the first half hour of the calorimetry test was discarded to minimize the error induced by the difference in the initial temperature of the paste. The temperature of the calorimeter chamber was regulated at 23 °C for all groups.

3.3.2.2.3.1 0.5% Slaked Lime Concentration

Experimental results shown in Chapter 2 suggest that it only takes less than 3 min to fully carbonate the 0.5% slaked lime slurry. Therefore, further carbonating the slurry after 3 min will convert more of the produced CaCO_3 into $\text{Ca}(\text{HCO}_3)_2$ and stabilize it. This will reduce the available seeding sites for hydration products provided by CaCO_3 . As a result, promoting effect of the pre-carbonation on the hydration of cement diminishes as shown in Figure 3.7(a.). This figure shows that carbonating the slurry with 20 min made the hydration rate of the pre-carbonated cement paste even lower than that of the control group. This is because most of the produced CaCO_3 nanoparticles were converted into $\text{Ca}(\text{HCO}_3)_2$, and that the reaction between $\text{Ca}(\text{HCO}_3)_2$ and CH in the fresh cement paste can delay the formation of new precipitates of the hydration products of the cement.

3.3.2.2.3.2 1% Slaked Lime Concentration

Calorimetry testing results for the cement pastes produced by carbonating 1% slaked lime are shown in Figure 3.7(b). It can be seen that the hydration of all pastes was promoted by the pre-carbonated slurry for all three durations of carbonation. The hydration rate of the paste was

improved with the duration of carbonation increased from 10 min to 15 min. However, further increasing the duration of carbonation to 20 min, the hydration rate became lower. This can be attributed to that some CaCO_3 particles were converted into $\text{Ca}(\text{HCO}_3)_2$ by the carbonic acid induced by CO_2 . This not only reduced the surface area as seeding sites for hydration products, but also reduced the availability of Ca^{2+} in the paste due to the reaction between $\text{Ca}(\text{HCO}_3)_2$ and CH. The aggregation of produced CaCO_3 nanoparticles could be another reason. As a result, the hydration rate of the paste was lower than the one carbonated for 15 min. Figure 3.7(b) clearly suggests that there exists an optimal duration of carbonation, by which the highest promotion of the hydration of cement can be achieved.

3.3.2.2.3.3 3% Slaked Lime Concentration

Figure 3.7(c.) shows the calorimetry results of cement pastes with 3% slaked lime carbonated for three different durations. Similar to previous cases, the hydration rate of all the cement pastes were significantly improved. The accumulated thermal energies released during the hydration of the pastes were increased by 16%, 17% and 10% at 72 h for 10 min, 15 min and 20 min carbonation, respectively. However, the peak of the thermal power in these pre-carbonated pastes appears earlier than that of the control one, suggesting that dormant stage of the paste was reduced by the pre-carbonation. This phenomenon was not observed in the pastes with lower concentration of slaked lime (0.5% and 1%). Because there was no bicarbonate ion existing in 3% group especially with 10 min and 15 min carbonation to delay the acceleration effect caused by the produced CaCO_3 nanoparticles. Another reason can be because 3% slaked lime cannot be fully carbonated using the present CO_2 bubbling method with the given carbonation duration. As a result, there should be a significant amount of un-carbonated slaked lime existing in the pre-carbonated slurry. It was speculated that this residual slaked lime is responsible for the shorter

dormant period of the cement pastes due to their high pH value which can accelerate the dissolving of cement clinker. To test this hypothesis, cement paste added with 3% slaked lime without carbonation was produced and their calorimetry test result is presented in Figure 3.7(d). It can be seen clearly that the dormant period of the cement paste was reduced by the addition of un-carbonated slaked lime. In addition, the hydration rate and the accumulated hydrate heat released by the paste was reduced by the slaked lime. Therefore, Figure 3.7(d) also suggests that carbonating the slaked lime is necessary to promote the hydration of the cement paste and the reason responsible for this promotion should be new CaCO_3 particles produced during the pre-carbonation.

Figure 3.7(c) also shows that the optimal promotion result was achieved by carbonating the slaked lime for 15 min. If the carbonating duration was increased to 20 min, hydration rate was slightly reduced, which is very similar to the case when 1% of slaked lime was used.

3.3.2.3 Summary of Calorimetry Study

Comprehensive calorimetry test program has been carried out to examine the effect of pre-carbonation on the hydration of cement paste. Some conclusions can be drawn based on obtained testing results:

1. Neither limestone powders nor un-carbonated slaked lime can promote the hydration of cement.
2. Significant improvement on both the rate and the total released energy of cement hydration can be significantly improved by pre-carbonating the slaked lime slurry. New surface area provided by the in-situ produced CaCO_3 nanoparticles is the major reason responsible for this improvement.

3. Better promotion results on the hydration of cement can be achieved by sonicating the slaked slurry during the carbonation than by magnetically stirring. This is because sonicating can disperse the slaked lime and produced CaCO_3 particles better.
4. Carbonating the slaked lime at higher temperature can lead to higher hydration rate and total released hydration energy of cement.
5. There exists an optimal duration of carbonation. By using this duration to carbonate the slaked lime slurry, highest improvement on hydration rate and total released energy can be achieved.

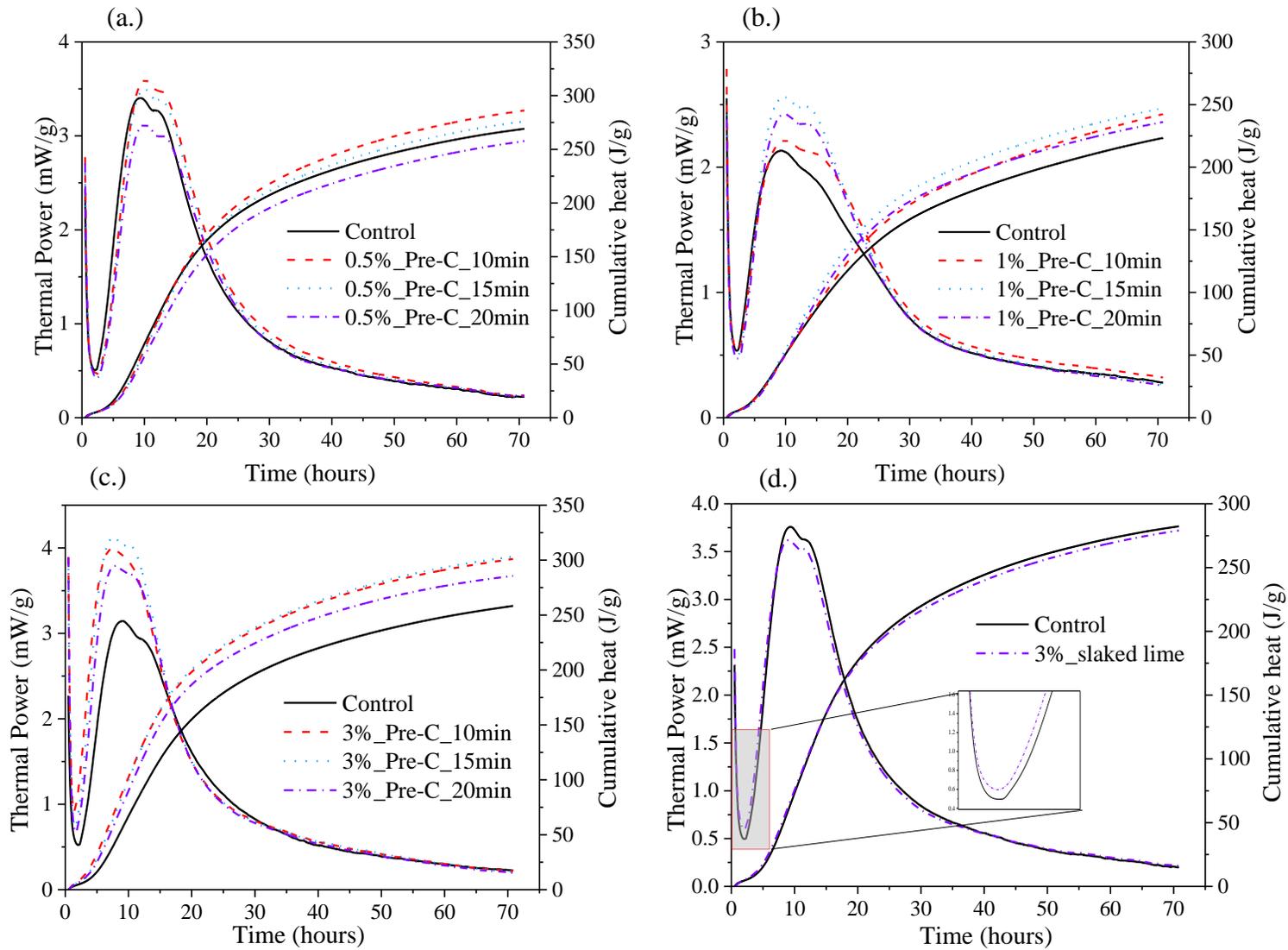


Figure 3.7. Comparison of hydration heat of cement pastes pre-carbonated with different carbonation durations and concentrations of slaked lime: (a.) 0.5% slaked lime, (b.) 1% slaked lime, (c.) 3% slaked lime, (d.) 0 min carbonation for 3% slaked lime

3.3.3 XRD

As mentioned in Chapter 1, calcium carbonate particles can not only serve as nucleation sites, but also influence the distribution of lime, alumina and sulfate, and thereby alter the mineralogy of the hydrated cement pastes. The final reaction products are mainly determined by the molar ratio of $\text{CO}_2/\text{Al}_2\text{O}_3$ and $\text{C}_3\text{A}/\text{SO}_3$, as shown by thermodynamic simulation in Figure 1.2. From XRF analysis, the cement used in this study has 4.89% Al_2O_3 , which is equal to 0.479 mol/kg. Carbonating 1% slaked lime slurry can introduce approximately 0.07 mol/kg carbonate into the cement paste with w/c ratio of 0.5. In this paste, the $\text{CO}_2/\text{Al}_2\text{O}_3$ ratio is only 0.15, which is much smaller than 0.66, the limit ratio for chemical reaction between the carbonate and the hydration products of cement. Above this ratio, CaCO_3 will only function as fillers, diluting the binding effect of OPC.

To estimate this potential reaction, XRD analyses were carried out to study the hydration product of cement paste produced by carbonating 1% and 3% slaked lime at 23 °C for 15 min and 20 min, respectively. The XRD patterns of the cement pastes produced with/without using carbonation method at 4 d are shown in Figure 3.8. It can be seen that more ettringite was produced in the pre-carbonated groups, which is in agreement with the results of thermodynamic simulation discussed in Chapter 1. Because of the limitation of XRD equipment we have, the peaks for different phases of AFm were not detected. Therefore, TGA was carried out to confirm this observation.

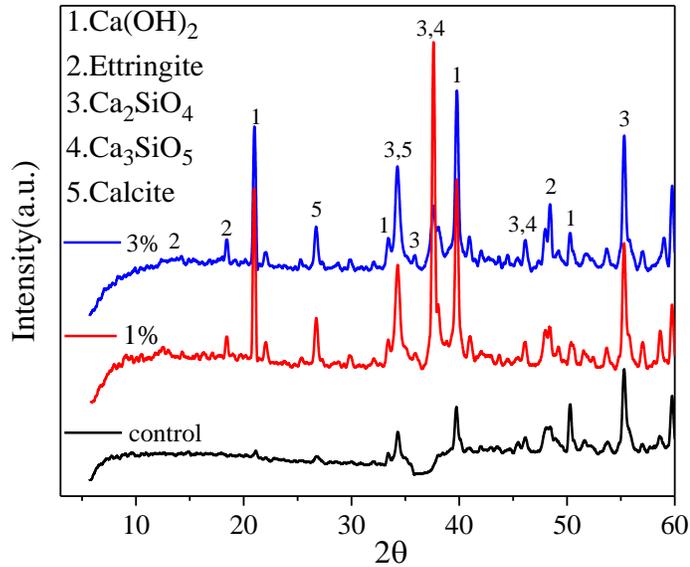


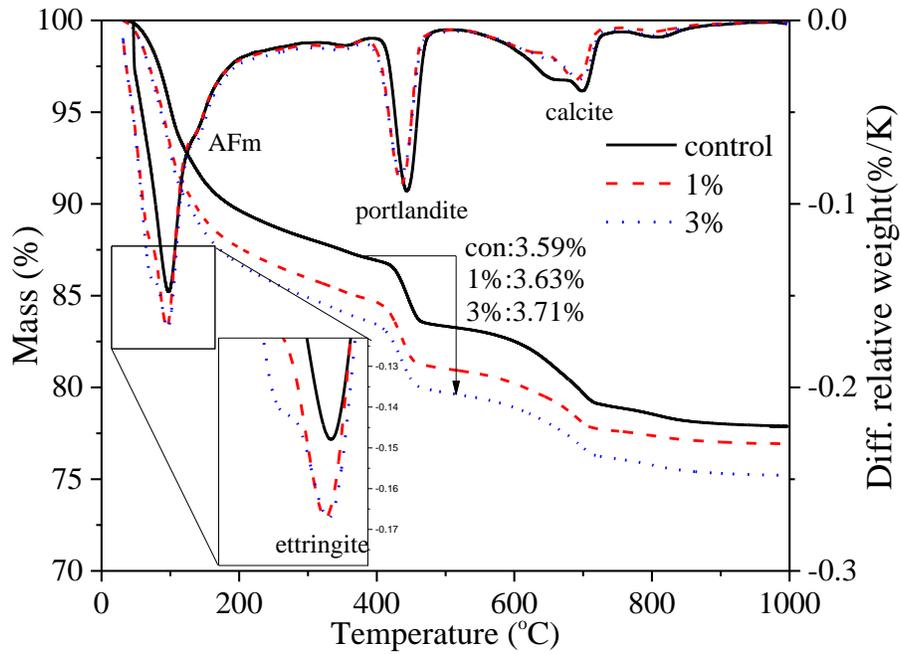
Figure 3.8. XRD patterns of cement pastes with pre-carbonation method

3.3.4 Thermogravimetric Analysis (TGA)

TGA results of the cement pastes produced with and without using pre-carbonation method at ages of 4 and 8 d were presented in Figure 3.9 and Figure 3.10, respectively. Here, the pre-carbonated pastes were produced by carbonating the 1% and 3% slaked limes for 15 min and 20 min, respectively. Two different temperatures were used to carbonate the slurries.

As shown in these figures, three main peaks appear on the derivative mass loss (DTG) graph of these samples, corresponding to the decomposition of ettringite, CH and calcite, respectively. As marked in these figures, the typical decomposition temperature ranges for ettringite, AFm, CH and calcite are 80 °C-130 °C, 180 °C-200 °C, 400 °C-500 °C, and 680 °C-760 °C, respectively [131–134]. The weight loss of C-S-H mainly starts at 105 °C and mainly occurs at 120 °C -160 °C [134]. Clearly, both the C-S-H and ettringite decompose when temperature is within 105 °C and 130 °C, making it difficult to estimate the exact weight loss of ettringite. Nevertheless, the weight loss between 80 °C and 105 °C can be considered mainly due to ettringite.

(a.)



(b.)

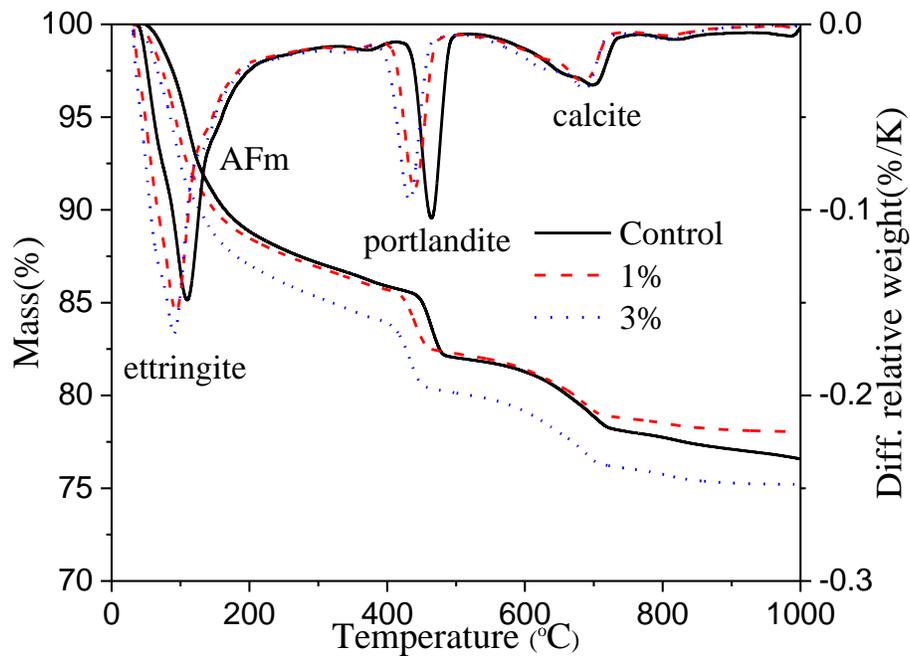


Figure 3.9. TGA results of cement pastes produced by pre-carbonating slaked lime slurry at temperature at 4 d: (a.) 23 °C; (b.) 7 °C.

The calculated weight losses of ettringite, AFm, portlandite and calcite are presented in Table 3.6 based on the temperature range mentioned above. It can be seen that more ettringite was produced in all pre-carbonated samples, which is in good agreement with the XRD results shown

in Figure 3.8. This is because the CaCO_3 particles produced by the pre-carbonation alter the mineral composition in hydrated cement paste. This is also in agreement with the thermodynamic simulation [72], which shows that more carbonates lead to produce more ettringite. Less calcite was found in the pre-carbonated samples, which is presumably due to formation of hemicarboxylate/monocarboxylate phases. No significant difference with respect to the content of AFm (including both monocarboxylate and monosulfate) was found among these samples.

Table 3.6. The calculated weight losses of cement pastes at 4 d

Temperature	Specimen	Weight loss (%) related to the decomposition of			
		Ettringite	AFm	CH	Calcite
7°C	Control	2.80	0.58	3.85	1.52
	1%	3.71	0.45	3.45	1.05
	3%	3.95	0.49	3.78	1.16
23°C	Control	4.81	0.47	3.58	1.56
	1%	5.26	0.46	3.63	1.12
	3%	5.50	0.50	3.70	1.29

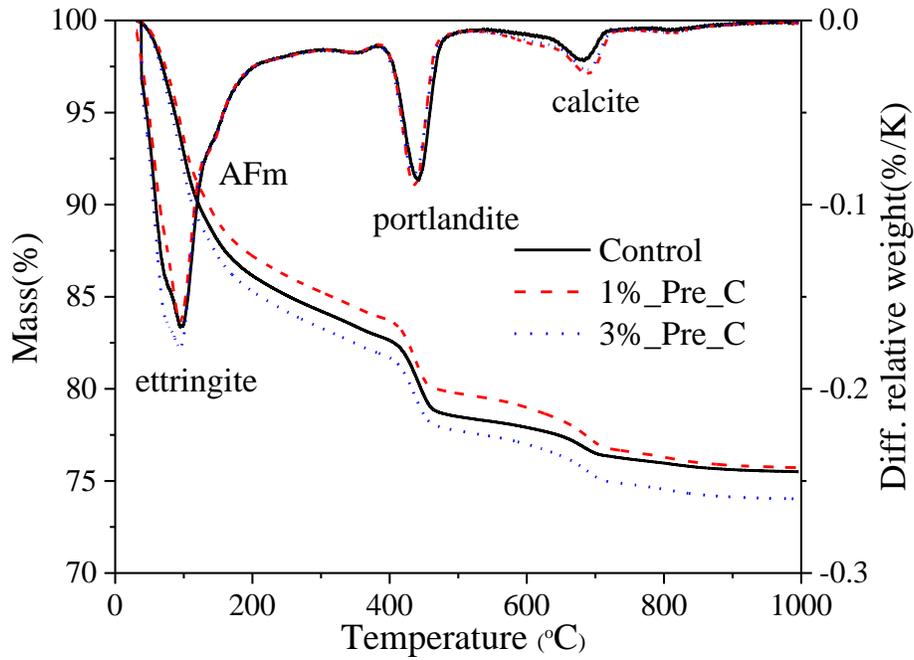
The amount of CH in cement paste at early age depends on the hydration degree of C_3S . More CH in the sample means more C-S-H produced. Compared with their control groups, CH content in the paste samples was reduced by pre-carbonation at 7 °C, but increased by the pre-carbonation at 23 °C. It is easy to understand that CH content in the paste was reduced by the pre-carbonation at 7 °C, because the reaction between CH and $\text{Ca}(\text{HCO}_3)_2$ consumed some of CH. However, pre-carbonation can promote the hydration of cement, which will produce more CH than the control group. If this extra amount of CH produced by the promoted hydration

surpasses the amount of CH consumed by the $\text{Ca}(\text{HCO}_3)_2$, there will be more CH in the pre-carbonated paste than in the control one, as demonstrated by the paste produced by carbonating the slaked lime slurry at 23 °C. This can be confirmed by the calorimetry results (Figure 3.6). As shown in the figure, the peak of C_3S is much higher than that in the control group, suggesting that more portlandite was produced by the pre-carbonation at 23 °C.

The TGA results of the cement paste samples at 8 d are shown in Table 3.7. Compared to the samples at 4 d, CH contents in these samples are higher, especially the one produced with pre-carbonated 1% slaked lime at 7 °C (which has highest amount of bicarbonate). Such difference is clearly due to the hydration of cement, which produces more CH, compensating the loss of CH at the early age due to the reaction between the CH and $\text{Ca}(\text{HCO}_3)_2$.

The ettringite of all groups produced by pre-carbonating at 23 °C is lower at 8 d than at 4 d. This can be attributed to the conversion from ettringite to monosulfate or monocarbonate. Numerous studies showed the addition of calcite can prevent the transformation from ettringite to monosulfate [135–137]. Due to the limitation of XRD instrument we used, the peaks of different AFm phases, however, were not detected. Further works need to be done to compare the content of monosulfate and monocarbonate/hemicarbonate in the pastes.

(a.)



(b.)

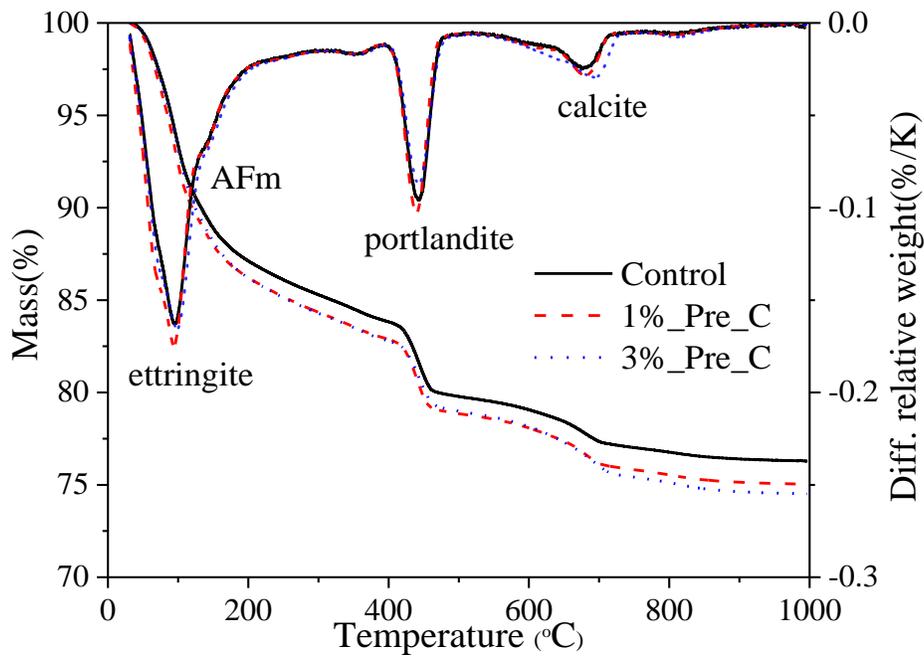


Figure 3.10. TGA results of cement pastes produced by pre-carbonating slaked lime slurry at temperature at 8 d: (a) 23 °C; (b) 7 °C.

Table 3.7. The calculated weight losses of cement pastes at 8 d

Temperature	Specimen	Weight loss (%) related to the decomposition of			
		Ettringite	AFm	CH	Calcite
7°C	Control	3.90	0.54	4.04	0.82
	1%	4.19	0.54	4.02	0.89
	3%	3.92	0.58	3.80	1.24
23°C	Control	3.92	0.58	4.14	0.77
	1%	3.91	0.56	4.06	1.12
	3%	4.33	0.57	4.07	0.99

3.3.5 SEM Analysis

The microstructure of cement pastes produced with pre-carbonation method was carried out using SEM with two purposes: identifying CaCO_3 nanoparticles in the paste to directly confirm that nanoparticles can be produced by the pre-carbonation method and detecting difference in microstructure induced by the pre-carbonation to gain deep understanding of the working mechanism of the pre-carbonation method. However, it is difficult to differentiate calcium carbonate particles from other cement hydration products due to its small size. Back scatter mode is not useful in this case because C is close to O in terms of atomic weight. The representative microstructures were obtained through secondary electron microscopy for the cement paste specimens made without using (Figure 3.11(a)), and using pre-carbonation technique (Figure 3.11(b)), respectively.

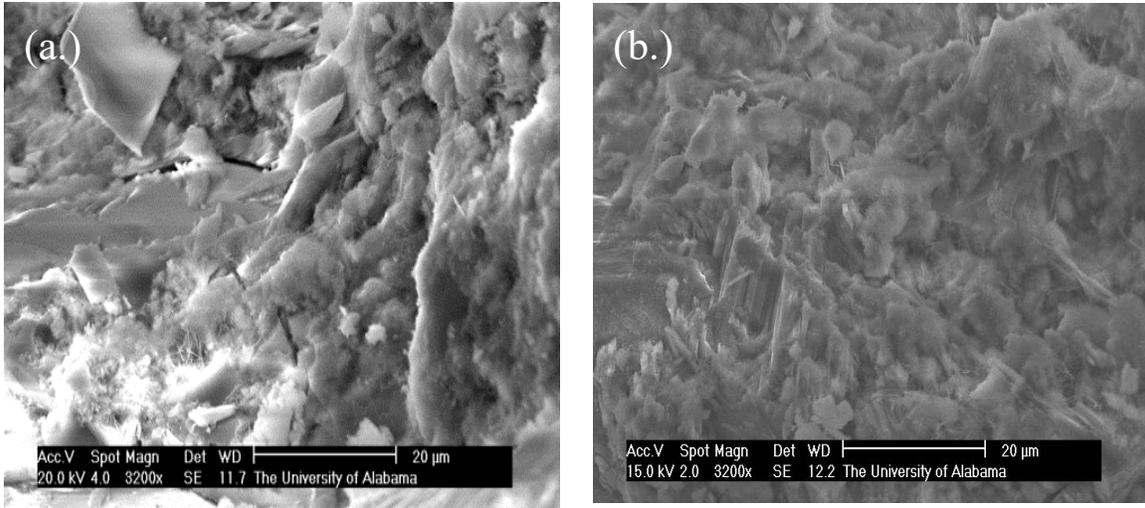


Figure 3.11. SEM images of mortar specimens produced with and without using pre-carbonation method: (a.) control specimen; (b.) pre-carbonated specimen

It can be found that the microstructure of the pre-carbonated mortar (Figure 3.11(b)) is denser than that of the control specimen, as shown in Figure 3.11(a). Micro-cracks can be observed existing in the control specimen. No such micro-cracks can be observed in the pre-carbonated specimen. This is likely a result of the reaction between CaCO_3 and aluminate. As mentioned earlier, the addition of CaCO_3 can modify the hydration of C_3A [135,136]. With fixed ratio of $\text{SO}_3/\text{Al}_2\text{O}_3$, more carbonate can increase the volume of the hydration products of the cement through producing more ettringite, as revealed by the XRD/TGA results shown in Figures 3.8-3.10. As a result, the microstructure of the pre-carbonated mortar is denser.

Extensive studies show that nanoparticles can reduce the porosity of cement-based material by acting as nanofillers and accelerating the formation of C-S-H [12,13]. The CaCO_3 particles produced by the pre-carbonation technique have an average size of 130 nm from Brunauer–Emmett–Teller (BET) analysis, which is much smaller than cement particles. Therefore, they can also fill the voids in cement paste to further densify the microstructure of the mortar sample, as shown in Figure 3.12. This figure shows a polished surface of the cement paste made by using pre-carbonation method. Small particles with size around 100 nm were exposed in the gap of

cement particles. These particles have a trigonal-rhombohedral shape, which is typical for calcite crystal. Due to the size of these particles, energy-dispersive X-ray spectroscopy is not able to give a convincing result about the element composition of these particles.



Figure 3.12. Possible calcite nanoparticles in a polished cement paste sample

3.3.6 Porosity and Density

Helium porosimetry test was carried out on a control cement paste sample produced without using pre-carbonation and a pre-carbonated one produced by carbonating 1% slaked lime for 15 min at 23 °C. Testing result shows that pre-carbonation slightly reduces the porosity of the produced paste sample, from 30.8% of the control to 30.3% of the pre-carbonated sample. The small amount of reduction in porosity is possibly due to the limited amount of calcium carbonate produced by pre-carbonating the slaked lime slurry. The speed to carbonate the slaked lime slurry is limited by the low solubility of $\text{Ca}(\text{OH})_2$ and CO_2 in water. Longer duration of carbonation can produce more CaCO_3 precipitates, but will lead to excessive aggregation of the produced nanoparticles, which will negatively affect the promotion effect on the hydration of cement. Therefore, the amount of CaCO_3 nanoparticles produced by the proposed carbonating method is very limited with current experimental setup.

The average bulk densities of 3 duplicated pastes produced with and without using pre-carbonation are 1.607 g/cm³ with a variation 0.046 g/cm³ and 1.561 g/cm³ with a variation 0.019 g/cm³, respectively. Pre-carbonation slightly increases the bulk density of the paste by 3% in comparison with the control group, suggesting that pre-carbonation can produce more compacted microstructure. Another possible reason for this increase in density is that more ettringite was produced and stabilized in the paste by the pre-carbonation. In the control group, some of the ettringite will transform into monosulfate [135], which has a density of 0.68 kg/m³, much lighter than that of ettringite (1.75 kg/m³) [138].

3.3.7 Mechanical Properties

Calorimetry tests already show that pre-carbonation can significantly improve the early age hydration of OPC. It is anticipated that such enhancement in hydration of cement can improve the mechanical properties of the produced cement mortar or concrete.

3.3.7.1 Compressive Strength

Figure 3.13 compares the compressive strengths of cement mortars produced by different methods detailed in Section 3.2. The compressive strength of the samples produced using pre-carbonation method was higher than the control one by 13%, 16%, and 16%, at the ages of 3, 7, and 28 d, respectively. Here, the pre-carbonation was carried out at 7 °C. If only 1% slaked lime was added without pre-carbonation, the induced improvement on the compressive strength of the mortar is negligible. This suggests that pre-carbonation is necessary to enhance the strength of the mortar. This finding agrees very well with the calorimetry test results. Another possible reason responsible for the strength enhancement in the pre-carbonated cement mortar samples is that more ettringite was produced in the sample, as revealed by the TGA results shown in Figures 3.9 and 3.10. The compressive strength of the mortar with 1% of OPC replaced by limestone powder (limestone group in Figure 3.13) has a strength even lower than the control

group. According to thermodynamic simulation [72], the strength of this mortar is anticipated to be higher than the control one since more ettringite can be produced by adding limestone powders. The observed reduction in strength of this mortar can be attributed to the low reactivity of the limestone powders.

Figure 3.13 demonstrates that highest improvement can be achieved by the pre-carbonation method, and this improvement cannot be achieved by simply replacing the cement with slaked lime or limestone powders.

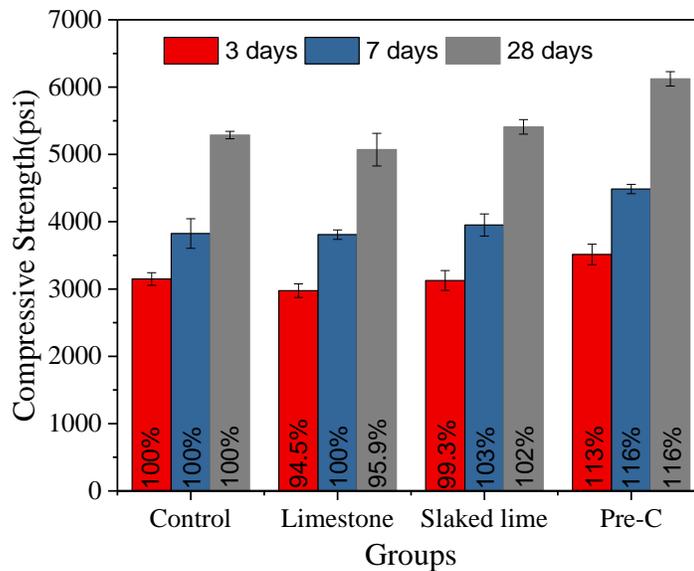


Figure 3.13. Compressive strengths of cement mortars produced by different methods

The effect of pre-carbonation conditions on the compressive strengths of cement mortars are shown in Figure 3.14-Figure 3.17. Four major conditions considered here are dispersing method, slaked lime content, carbonation duration, and carbonation temperature. All pre-carbonated specimens shown in these figures, were prepared with carbonation temperature 23 °C if not specified. In addition, the effectiveness of the pre-carbonation method on mortar with different w/c ratios was also investigated.

3.3.7.1.1 Dispersing Method

Figure 3.14 compares the compressive strength of pre-carbonated cement mortar made with two different dispersing methods. It can be seen that higher strength can be achieved by sonicating the slaked lime slurry during carbonation with an ultrasonic bath. The compressive strength of the mortar samples was enhanced by 22%, 19% and 13%, at ages of 3, 7, 28 d, respectively; While stirring the slurry during carbonation using a magnet stir can only enhance the compressive strength of the mortar by 16%, 11% and 10%, at ages of 3, 7, 28 d, respectively. This is because the precipitates produced with ultrasonic bath have a higher surface area, providing more heterogenous nucleation sites for cement hydration. This result also agrees with calorimetry tests.

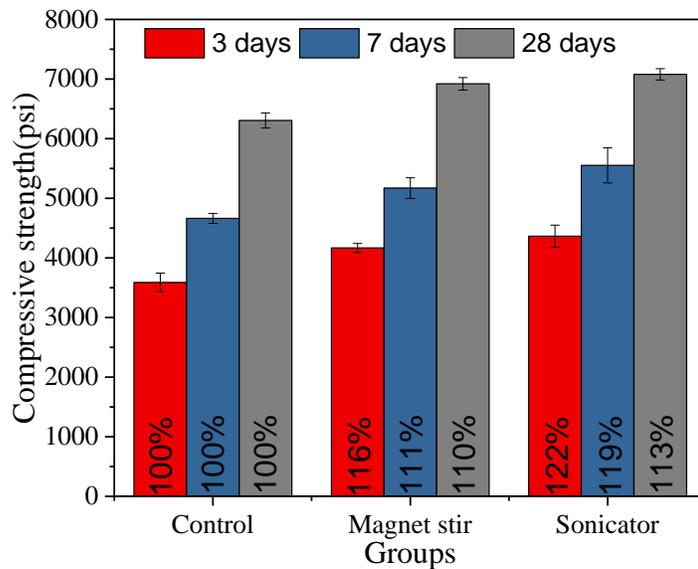


Figure 3.14. Effect of dispersing methods on the compressive strengths of pre-carbonated cement mortar samples

3.3.7.1.2 Effect of Carbonation Temperature

Figure 3.15 compares the compressive strength of cement mortar produced by carbonating 1% slaked lime at 7 °C and 23 °C. Although enhanced compressive strength can be achieved by both carbonating temperatures, strength development of the mortars exhibits different features.

At the lower carbonation temperature (7 °C), the cement mortar has higher compressive strength improvement at the ages of 7 and 28 d; while at the higher carbonation temperature (23 °C), the compressive strength improvement of the mortar is higher at the age of 3 d, but lower at the ages of 7 and 28 d. This suggests that the hydration of the cement at the early age of the mortar pre-carbonated at a higher temperature is faster than that pre-carbonated at a lower temperature, which is in agreement with the observation of the calorimetry tests, as shown in Figure 3.6. As discussed in detail in calorimetry test, more bicarbonate can be formed in the slaked lime slurry carbonated at 7 °C than at 23 °C. With more bicarbonate in the slurry, more calcium ions can be consumed to produce more CaCO₃ nanoparticles. This process can not only delay the formation of hydration products, but also weaken the precipitates on the surface of cement particles. These precipitates function as diffusion barrier to prevent further hydration of cement particles. By weakening this barrier, hydration of the cement can be facilitated at the later age, leading to higher compressive strength of the mortar samples.

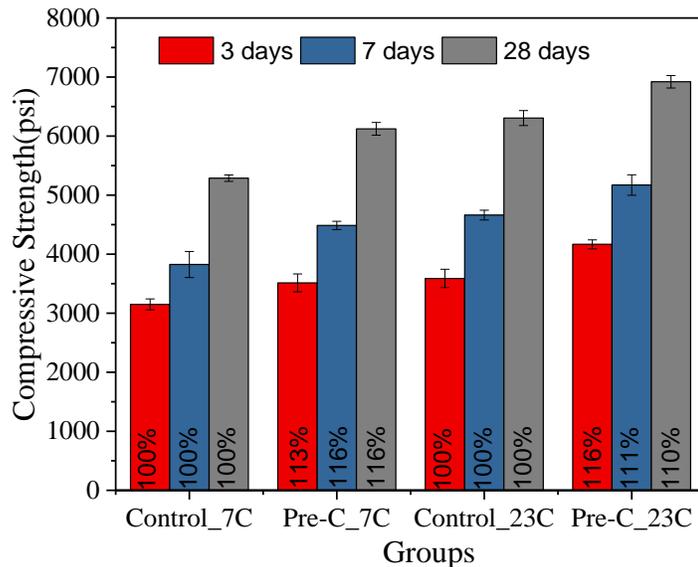


Figure 3.15. Effect of pre-carbonation temperatures on the compressive strengths of the mortar samples.

3.3.7.1.3 Effect of Slaked Lime Concentration

The slaked lime content plays an important role on the effectiveness of the pre-carbonation method. Higher concentrated slaked lime slurry is favorable to produce more calcium carbonate particles, providing more seeding sites for the hydration of the cement. This slaked lime slurry, however, requires longer carbonation duration due to the low solubility of carbon dioxide and the slaked lime in the water. With longer carbonation duration, the produced calcium carbonate nanoparticles will agglomerate and grow into larger particles, which significantly reduces the surface area of the calcium carbonate precipitates. In addition, our experimental study shows that slaked lime with higher concentration can result in worse workability. Therefore, there may exist an optimal content of slaked lime at which highest enhancement in mechanical properties can be achieved. To examine the effect of the concentration of slaked lime in the slurry, mortar samples were produced with slaked lime content from 1% to 5% (in weight of the water) pre-carbonated at 7 °C. Their compressive strengths are shown in Figure 3.16.

Figure 3.16 shows all pre-carbonated samples have higher strength than the control one. Clearly, strength improvement is not in proportion with the content of slaked lime. 5% slaked lime slurry actually produced the least improvement on the compressive strength. In addition, the measured strengths at 28 d of three duplicated samples scatter larger than other groups. This suggests that the quality of these mortar samples was not consistent due to the poor workability of the fresh mortar, which can be caused by the extended carbonation duration required to carbonate the 5% slaked lime slurry. With longer carbonation duration, CaCO_3 precipitates can aggregate, leading to poor dispersion of CaCO_3 particles and higher viscosity of the paste. For this reason, pre-carbonating 5% slaked lime slurry produced least enhancement of the strength.

Similar strength improvement from 3 d to 28 d was achieved by the rest two pre-carbonated groups. Compared with the group with pre-carbonated 1% slaked lime slurry, the compressive strength of the group with pre-carbonated 3% slaked lime slurry, exhibited larger variation, due to the poor workability of the fresh mortar.

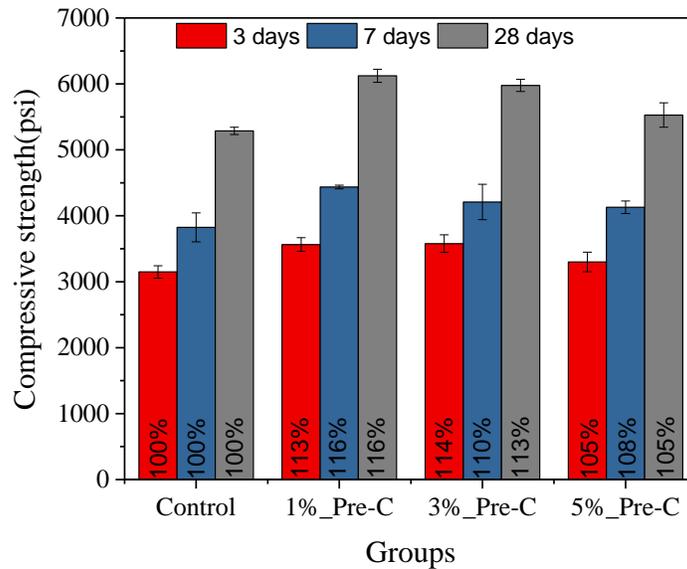


Figure 3.16. Effect of slaked lime concentrations on the compressive strengths of the cement mortar samples

3.3.7.1.4 Effect of The Carbonation Duration

The compressive strengths of mortar samples produced by pre-carbonating 1% slaked lime for three different durations are shown in Figure 3.17. It shows that pre-carbonating the slaked lime slurry can improve the strength of the sample. Slightly higher strength can be achieved by carbonating the slurry for 15 min than by 10 min. However, extending the carbonating duration to 20 min reduced the compressive strength enhancement, instead of further increasing the strength of the samples. This is in agreement with the calorimetry test shown in Figure 3.7(b). Two reasons are responsible for this slightly reduction in the compressive strength of the mortar when 20 min was used to pre-carbonating the slurry. Firstly, more bicarbonate was produced by the longer duration of carbonating which can delay the early age strength development.

Secondly, in-situ produced CaCO_3 particles aggregated into larger particles due to the longer carbonation duration, leading to less seeding site for the hydration of the cement.

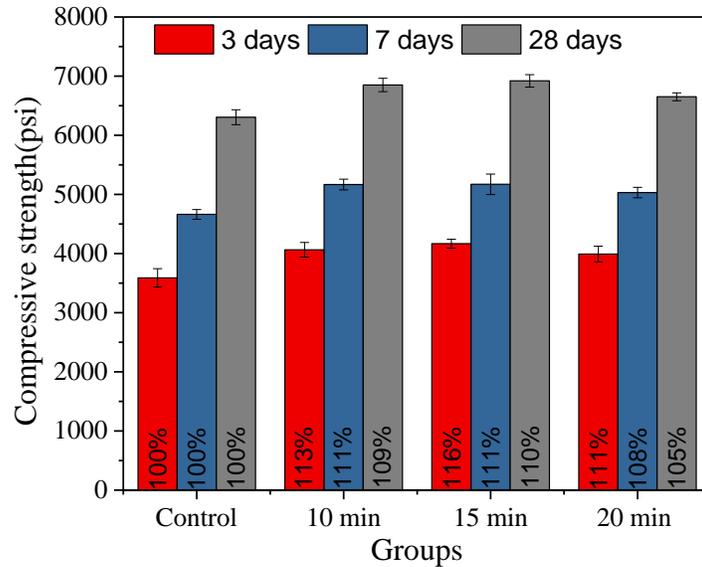


Figure 3.17. Effect of the carbonation durations on the compressive strengths of the cement mortar samples

3.3.7.1.5 Effect of w/c Ratio on the Effectiveness of the Pre-Carbonation Technique

Figure 3.18 compares the compressive strength of control cement mortar samples and pre-carbonated ones with different w/c ratios. Pre-carbonation was carried out on 1% slaked lime slurry at 7 °C. It can be seen that strength enhancement achieved by the pre-carbonation is dependent on the w/c ratio of the mortar. Higher strength improvement was achieved by the pre-carbonation method for the mortar sample with higher w/c ratio. At a low w/c ratio (0.3), only 4% improvement of the compressive strength at 28 d was achieved by the pre-carbonation. At 0.6 w/c ratio, the compressive strength of the mortar at 28 d was increased by 17%. This dependency on the w/c ratio may be attributed to the content of cement in the mortar samples. Cement content is higher in the mortar with lower w/c ratio. However, the same amount of pre-carbonated slaked lime was used in all the pre-carbonated samples. As a result, relatively lower

amount of carbonated slaked lime compared to cement was added into the mortar with low w/c ratio. As a result, strength enhancement induced by the pre-carbonation is lower.

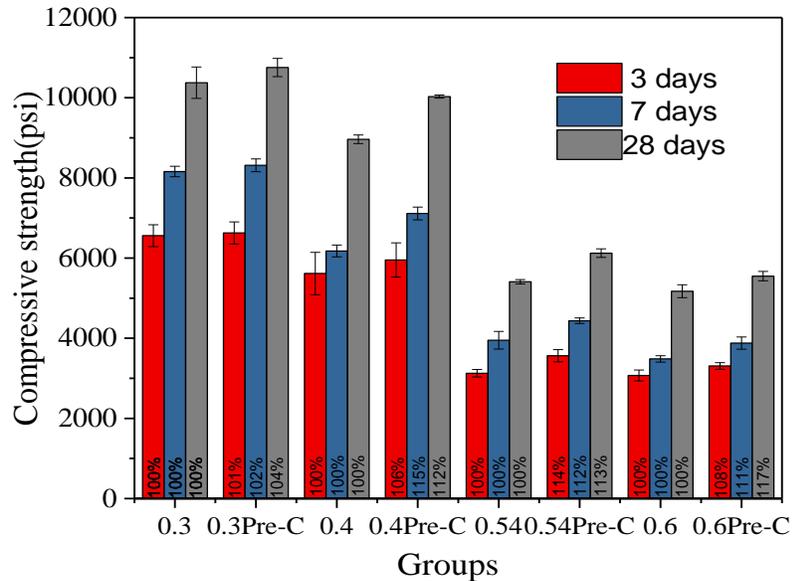


Figure 3.18. Effect of the pre-carbonation method on the compressive strengths of the cement mortar samples with different w/c ratios

3.3.7.2 Flexural Strength

Figure 3.19 compares the flexural strengths of a control mortar group and two groups produced through pre-carbonating slaked lime slurry at 23 °C at 7 and 28 d, respectively. By using pre-carbonated 1% slaked lime slurry, the flexural strength of the mortar sample was enhanced by 7% and 5% at 7 and 28 d, respectively. Similarly, flexural strength of cement mortars was enhanced by 8% and 5% at 7 and 28d, respectively, for the pre-carbonated group using 3% slaked lime slurry. This improvement on the flexural strength of the mortar samples is clearly due to the promoting effect of the pre-carbonation on the hydration of the cement.

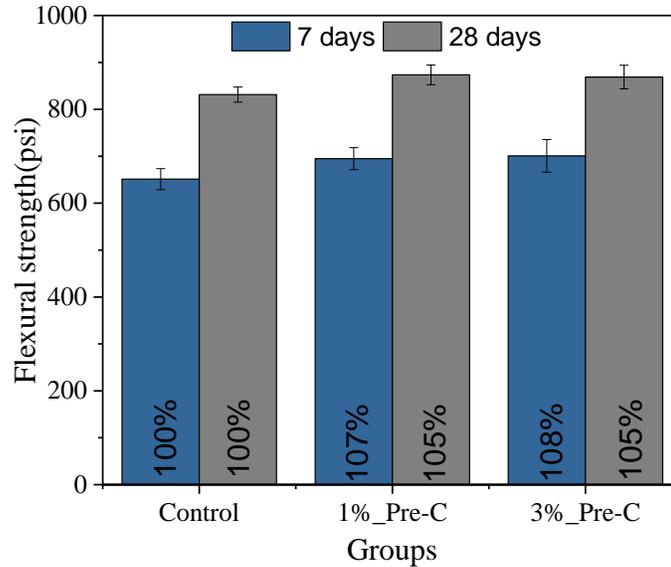


Figure 3.19. Flexural strengths of cement mortar samples produced with and without using pre-carbonation method

3.3.7.3 Modulus of Elasticity

The moduli of elasticity of the cement concrete samples produced with and without using the pre-carbonation method were measured, as shown in Figure 3.20. It can be seen that pre-carbonation technique enhanced the moduli of elasticity of the concrete samples by 4% and 2% at 3 and 28 d, respectively. It is reasonable to believe that this enhancement is resulted from the promotion effect on the hydration of cement induced by the pre-carbonation method.

It should be mentioned the carbonation duration for this test was 20 min, which include 15 min to fully carbonate the slaked lime slurry even for 1%. Because the percentage with respect to slaked lime concentration is by the weight of water, more water is needed for making concrete. In addition, current experimental setup was not prepared for large scale production. Hence, the carbonation duration was greatly increased. Further research is needed to study the mass production concrete with using pre-carbonation method.

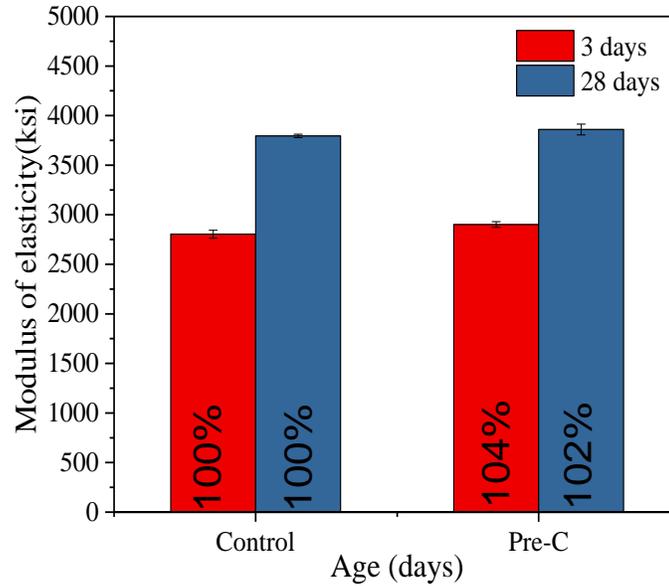


Figure 3.20. Improvement of the moduli of elasticity of concrete samples induced by the pre-carbonation method

3.3.8 Durability

The addition of nanoparticles often reduces the permeability of concrete due to their micro-filling effect, leading to a higher durability [12]. By using pre-carbonation method, CaCO_3 nanoparticles can be in-situ produced into cement mortar. In addition, the addition of carbonate can help stabilize ettringite, which can increase the total volume of hydrated phases and hence decrease the porosity of the mortar. Therefore, it is speculated that the permeability of the mortar samples produced using pre-carbonation method should be lower. To confirm this, water absorption test was carried out on the mortar samples produced with and without using pre-carbonation method since water absorption is linearly correlated with the permeability [124]. Sulfate resistance of mortars was also measured to examine whether pre-carbonation can improve the durability of the mortar.

3.3.8.1 Water Absorption Test

Figure 3.21 shows the rate of water absorption of cement mortars of three mortar groups, one control group and another two pre-carbonated groups produced by carbonating 1% and 3% slaked lime slurries.

It can be seen that the water absorption of the pre-carbonated group using 1% slaked lime does have lower permeability than the control group, as expected. Its water absorption is only 88% and 98% of that of the control one at 0.25 h and 24 h, respectively. However, water absorption of the pre-carbonated group using 3% slaked lime is 6% higher than that of the control group at 24 h. This unexpected increase in water absorption is possibly due to the poor workability of the mortar after carbonating the 3% slaked lime slurry. It is reasonable to conclude that permeability of mortar can be reduced by the pre-carbonation if no significant loss of workability occurs. This also agrees with the observation of the microstructure of the pre-carbonated mortar samples using SEM, as shown in Figure 3.11.

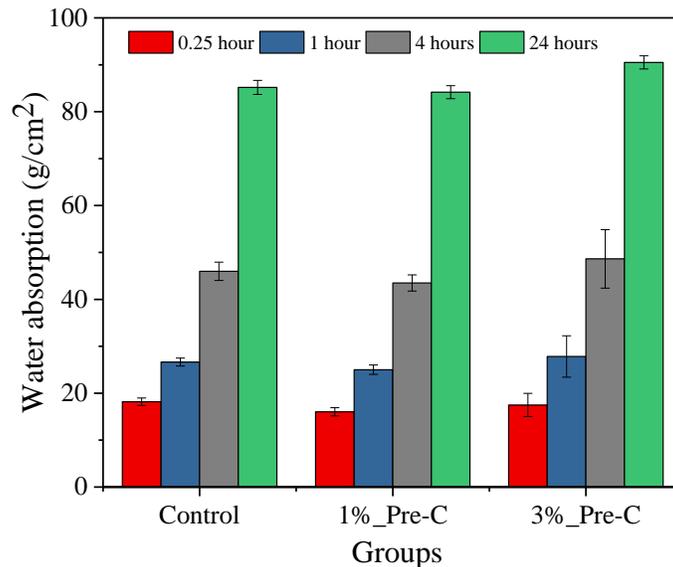


Figure 3.21. Water absorption of cement mortars produced with and without using pre-carbonation method

3.3.8.2 Sulfate Resistance Test

Theoretically, pre-carbonation can improve the sulfate resistance of the mortar samples for two reasons: 1) Reducing the permeability of the mortar so that less sulfate can migrate into the mortar sample; 2) Stabilizing ettringite to produce less monosulfate and monocarbonate, which are susceptible under sulfate attack [139]. To experimentally evaluate the potential of the pre-carbonation method on improving the sulfate resistance, expansions of mortar bars immersed in 50 g/L sulfate solution were measured, as shown in Figure 3.22. The expansion of these samples under sulfate attack is due to the formation of ettringite and gypsum [140]. It can be seen that the expansion of the pre-carbonated mortar with 1% slaked lime is lower than that of the control one, suggesting that pre-carbonating 1% slaked lime can improve the sulfate resistance of the mortar. However, the expansion of the pre-carbonated mortar bars with 3% slaked lime slurry is higher than that of the control one after 4 weeks, as shown in Figure 3.23. This unexpected feature is due to the higher permeability of the pre-carbonated sample with 3% slaked lime slurry as revealed in Figure 3.22, which is induced by the poor workability of the mortar.

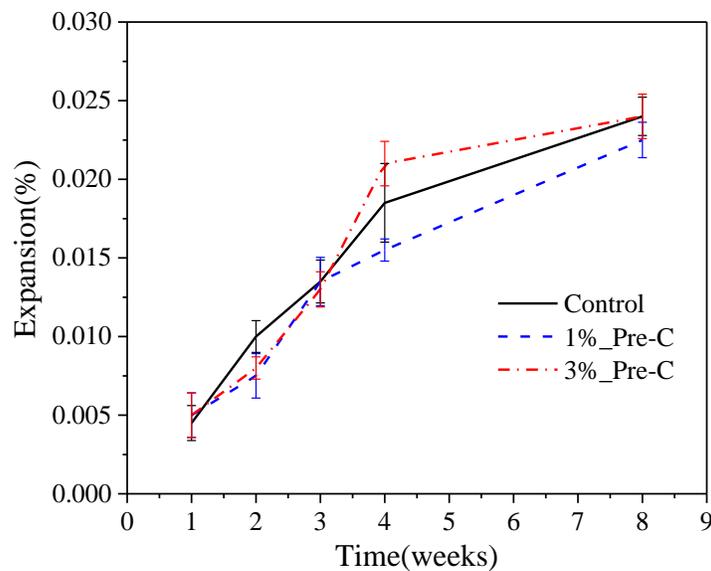


Figure 3.22. Expansions of mortar bars in 50g/L sodium sulfate solution.

3.3.9 Drying Shrinkage

Drying shrinkage of concrete is caused by loss of capillary water, which can cause an increase in tensile stress, leading to cracking of concrete. It has been shown that lower Ca/Si in C-S-H can result in higher drying shrinkage [141]. Pre-carbonation may reduce the Ca/Si of C-S-H since some calcium is consumed by bicarbonate. To evaluate whether pre-carbonation can increase the drying shrinkage of cement mortars, drying shrinkage tests were carried out on the control and the pre-carbonated samples, and testing results are shown in Figure 3.23. It can be seen that drying shrinkage of the pre-carbonated sample is smaller than the control one, especially at early age. This is anticipated since that small content of CO_2 is added and that the volume of CaCO_3 is larger than that of $\text{Ca}(\text{OH})_2$. TGA results also show that pre-carbonation helps produce more ettringite which occupies more space as compared to monosulfate. Thus, the drying shrinkage of pre-carbonated samples exhibited similar as compared to the control one.

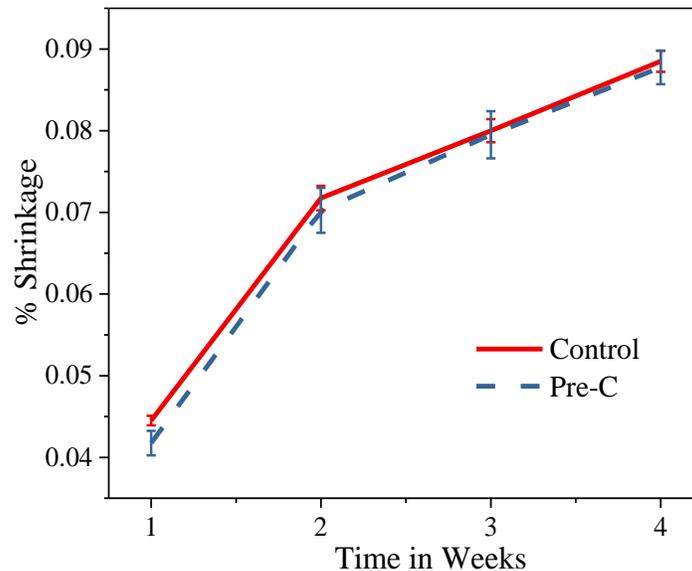


Figure 3.23. Drying shrinkage of cement mortars produced with/without using pre-carbonation method

3.3.10 Pore Solution

Pre-carbonation may lower the pH value of the slaked lime slurry which could interfere with the dissolution of cement particles or pose a risk of steel corrosion. However, due to the low solubility of bicarbonate and CO₂ in water, the effect of the pre-carbonation method on the pH value of the hardened cement mortar is negligible. To confirm this, the pH value of the pore solution of a control a pre-carbonated sample were extracted using method developed by Barneyback and Diamond [130] at the age of 3 d. The pH values for the dilute solution from the control and the pre-carbonated samples were measured as 12.79 and 12.78, respectively. Such a small difference in pH value of the pore solution suggests that pre-carbonation will not introduce any extra risk of steel corrosion.

3.4 Conclusions

In this chapter, the effects of carbonated slaked lime slurry on the behaviors of OPC-based cementitious materials were examined. It has been shown that pre-carbonation can promote the hydration of cement, and enhance both the mechanical properties and durability of the produced mortar/concrete samples. A few conclusions can be draw based on the findings of this chapter:

- Hydration of cement can be promoted by the pre-carbonation. The major reason responsible for this promotion is the extra heterogenous nucleation sites provided by the CaCO₃ nanoparticles in-situ produced by the pre-carbonation method.
- The dormant period of the cement hydration can be slightly extended by the bicarbonate in the pre-carbonated slaked lime slurry, especially at low carbonation temperature. Nevertheless, this extended dormant period can improve the late age strength of the mortar samples.

- TGA and XRD results showed that pre-carbonation does change the mineralogy of the hydrated cement. More ettringite was found in the samples produced by using pre-carbonation method.
- The porosity of the mortar sample produced with pre-carbonation is lower than that of the control group. This is resulted from higher volume of hydrated phase was produced in the pre-carbonated samples.
- Mechanical properties of the OPC-based cement mortar/concrete samples, including compressive strength, flexural strength, and modulus of elasticity, were enhanced by the pre-carbonation technique.
- Water absorption and sulfate resistance tests show that the durability of cement mortar was improved by the pre-carbonation technique. The denser microstructure of the pre-carbonated sample is the major reason for this improvement.
- Pre-carbonation can reduce the drying shrinkage of cement mortar, especially at early age.
- Pre-carbonation has negligible effect on the pH value of the pore solution in the mortar sample.
- The amount of slaked lime should be limited to a very low level (1%). Slaked lime with high concentration can induce serious loss of workability and require extended carbonation time.

CHAPTER 4

EFFECT OF PRE-CARBONATION TECHNIQUE ON THE PROPERTIES OF METAKAOLIN/FLY ASH BLENDED OPC MORTAR

4.1 Introduction

Chapter 3 demonstrates that the performance of OPC-based mortar/concrete can be improved by carbonating slaked lime slurry through in-situ production of CaCO_3 nanoparticles, which not only providing seeding sites for hydration products, but also tuning the mineralogy of the hydration products.

In this chapter, we extended the pre-carbonation method to OPC-supplementary cementitious material (SCMs) blended cement mortar/concrete. Two commonly used SCMs, fly ash and metakaolin were considered in this study because of the synergistic effect between these two SCMs and CaCO_3 [142]. By replacing OPC with Al_2O_3 -rich SCMs, the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio of the blended cement can be reduced, and more ettringite and AFm phases can be produced after hydration. The effect of CaCO_3 on stabilization of ettringite is more pronounced in this blended cement than in pure OPC cement [143].

4.2 Materials and Methods

4.2.1 Materials

The SCMs, metakaolin and fly ash, were obtained from Powerpozz company and the James H. Miller, Jr. Electric Generating Plant (owned by Alabama Power/Southern Company), respectively. Class C fly ash was chosen to replace OPC because of its high content of calcium which can compensate the Ca^{2+} ions consumed by bicarbonate ions produced by the pre-

carbonation method. The chemical compositions obtained from X-ray fluorescence (XRF) of these two SCMs are presented in Table 4.1. The fine aggregates used in this research is river sand with bulk specific gravity of 2.70 and water absorption capacity of 0.95%. All the aggregates were oven-dried for 12 hours at 110 °C before mixed with other ingredients.

Table 4.1. Chemical composition of fly ash and metakaolin (%)

Oxide Composition	Class C fly ash	Metakaolin
SiO ₂	34.7	59.4
TiO ₂	1.4	0.5
Al ₂ O ₃	18.2	30.8
Fe ₂ O ₃	5.4	1.4
MgO	5.9	2.2
CaO	26.5	0.1
Na ₂ O	2.2	2.7
K ₂ O	0.4	1.3
LOI	0.66	0.68

4.2.2 Mix Proportions

Four groups of cement mortar samples were made to investigate the effect of pre-carbonation method on the compressive strength of the metakaolin blended cement mortar, as shown in Table 4.2. 20% cement was replaced by the metakaolin for all control and pre-carbonated mortars. The control group of cement mortars were prepared with water to cementitious materials ratio (w/cm) of 0.5 without using pre-carbonation method. Groups 1% and 3% were made by pre-carbonating the slaked lime slurries with a concentration of slaked lime as 1% and 3% of the mixing water, respectively. Superplasticizer was used to tune the workability of the mortar samples to ensure the same workability was achieved by both the control and the pre-carbonated groups.

To make fly ash-OPC blended mortar, 30% OPC was replaced by class C fly ash for all control and the pre-carbonated groups, as shown in Table 4.3. The w/cm ratio was fixed at 0.5 for all groups. Similarly, control, 1%, and 3% groups were prepared based on the concentration of slaked lime slurry.

Table 4.2. Mix proportions for metakaolin blended cement mortars produced with/without using pre-carbonation method (lbs/yd³)

Constituent	Control	1%	3%
Cement	485.6	483.2	478.3
Metakaolin	121.4	120.8	119.6
Water	303.5	303.5	303.5
River Sand	1530.0	1530.0	1530.0
Slaked Lime	-	3.0	9.1
Superplasticizer	3.3	3.7	3.7
Pre-Carbonation	-	Yes	Yes

Table 4.3. Mix proportions for fly ash blended cement mortars produced with/without using pre-carbonation method (lbs/yd³)

Constituent	Control	1%	3%
Cement	424.9	422.8	418.5
Fly ash	182.1	181.2	179.4
Water	303.5	303.5	303.5
River Sand	1530.0	1530.0	1530.0
Slaked Lime	-	3.0	9.1
Pre-Carbonation	-	Yes	Yes

4.2.3 Characterization Methods

4.2.3.1 Isothermal Calorimetry

To understand how pre-carbonation alters the hydration kinetics of metakaolin/fly ash blended cement pastes, their hydration heats were measured based on ASTM C1679 and ASTM C1702 [118,119]. To this end, a few pre-carbonated paste samples were prepared with the

carbonated slaked lime slurry. The slaked lime slurry was produced by first dissolving slaked lime into 500 g deionized water, and then stirring for 3 min. Two concentrations of slaked lime, 1% and 3%, were used to make the slurry so that the effect of the amount of slaked lime on the hydration of the blended cement paste can be evaluated. The mixed slurry was then carbonated through bubbling CO₂ for certain time. Both the control and the pre-carbonated specimens were made at the same initial mixing temperature. Before mixed with the carbonated slurry, 20% of 50 g cement was replaced by metakaolin and mixed for 3 min. Similarly, for fly ash, 30% of 50 g cement was replaced by fly ash and mixed for 3 min. The control paste specimen was produced by adding 50 g blended cement to 25 g deionized water and mixing for 2 min, before placed in the calorimeter. The pre-carbonated blended cement paste samples were produced in the same way as the control group except that pre-carbonated slaked lime slurries were used to replace mixing water. The hydration heat produced in the first 30 min of the test was deleted to minimize the effect induced by mixing cement paste. Measurements were recorded up to 72 h.

4.2.3.2 XRD with GADDS

It was reported the addition of limestone can change the mineralogy of the hydrated cement with metakaolin or fly ash [142,143]. The cement paste samples were prepared with the same proportion as those used in the calorimetry test. At 3 d, the cement paste was ground with a ceramic mortar before analysis. XRD patterns of all cement paste samples were obtained by scanning between 6° -66° with Bruker D8 Discover at a scanning rate of 10°/min using Cu K α radiation at 35 kV and 20 mA.

4.2.3.3 Thermogravimetric Analysis (TGA)

The metakaolin blended cement paste sample prepared in the same way as those used in calorimetry test was ground with a ceramic mortar and dried in the air. Then its weight was

measured using a Simultaneous Thermal Analyzer 8000 from 30 °C to 1000 °C at 10 °C per minute. Cement paste samples at 4 d were tested.

4.2.3.4 Strength Test

4.2.3.4.1 Compressive Strength

Compressive strengths of mortar samples were measured to estimate the potential of pre-carbonation on improving the strength of the metakaolin/fly ash blended cement mortar. To this end, mortar samples with six different mixes as shown in Tables 4.2 and 4.3 were produced and tested.

These mortars were cast into 50 × 100 mm cylinders according to ASTM C305 [121]. A vibration table was employed to consolidate the specimens. After stored in sealed plastic molds for 24 h, these specimens were demolded and cured in lime-saturated water at room temperature until the compression test was conducted. Before testing, all specimens were wiped with paper to remove water on the surface of specimens. The compressive strength of these specimens was measured at ages of 3, 7 and 28 d, respectively, using a Humboldt concrete compressor at a loading rate 35±7 psi. The average values of three duplicated specimens were reported.

4.2.3.4.2 Flexural Strength

Flexural strengths of mortar samples were measured to evaluate the effect of pre-carbonation on the flexural strength of metakaolin/fly ash blended cement mortars. 1% slaked lime by the weight of water were used to make mortar samples, as shown in Table 4.2 according to ASTM C348 [122]. The fresh mortars were cast into 40 × 40 × 160 mm steel prism molds and compacted with a vibration table. The molds were sealed with plastic sheet for 24 h before demolding. All the specimens were then cured in a moist chamber until the testing age. Similar

to the compressive tests, three duplicated specimens were measured at 7 and 28 d with a MTS QTest/25. The average of these three specimens were reported.

4.2.3.5 Durability Test

4.2.3.5.1 Water Absorption Test

The rates of water absorption of both control and pre-carbonated mortars with mix proportion shown in Table 4.2, were obtained using ASTM C1403 [125]. Three duplicated specimens with size of $50 \times 50 \times 50$ mm were cast and stored in a moist chamber covered by plastic sheet to prevent dripping water for 24 h before demolding. After that, all the specimens were demolded and cured in a sealed plastic bag at 23 °C. After 28 d, the specimens were dried in an oven at 110 °C for at least 24 h. When the difference between two successive measurements of the weight of the specimen were less than 0.2%, the specimens were taken out of the oven and cooled in the ambient environment. After measuring the width and length of the soaking surface and the initial weight of the specimens, all of them were immersed 3 mm into water. The weight of these immersed mortars was measured at 0.25, 1, 4, and 24 h. The surface water of specimens was wiped down with damp cloth before each weight measurement.

4.2.3.5.2 Sulfate Resistance Test

Sulfate resistance of the metakaolin blended cements was measured using mortar bars prepared based on ASTM C1012 with dimension of $1 \times 1 \times 11$ in. [126]. The water to cementitious materials ratio of the mortar is 0.485 and the ratio between river sand and cement is 2.75 for both the control and the pre-carbonated specimens. After casting, the specimens were initially cured in a sealed container and placed into an oven at 35 ± 3 °C for 24 h. Then the specimens were demolded and cured in saturated lime water at 23 °C until an average compressive strength of 2850 psi measured by cubic specimens made in same batch was reached.

After recording the initial length, all these mortar bars were submerged in the 50 g/L sodium sulfate solution which was produced by dissolving anhydrous sodium sulfate purchased from VWR with a purity of 99% into deionized water. The lengths of these cement mortar bars were measured using a comparator after 1, 2, 3, 4, and 8 weeks.

4.3 Results and Discussion

4.3.1 Isothermal Calorimetry

4.3.1.1 Effect of Pre-carbonation on Hydration Heat of metakaolin blended OPC

Figure 4.1 shows the calorimetry result of metakaolin blended cement pastes with and without using pre-carbonation method. 1% and 3% slaked lime slurries were carbonated at 23 °C for 10 min and 15 min, respectively. Both pre-carbonated metakaolin blended pastes exhibit higher and stronger peaks of the hydration of tricalcium silicate (C_3S) and tricalcium aluminate (C_3A), as shown in Figure 4.1. This figure clearly suggests that the rate of hydration of metakaolin blended OPC was promoted by the pre-carbonation. Similar to the case of using pure cement studied in previous chapter, this promotion effect is attributed to the higher surface area induced by nanoparticles in-situ produced by the pre-carbonation method. Unlike the calorimetry curve of the pure cement paste, the peak of C_3A hydration of the pre-carbonated blended cement pastes is higher than that of C_3S . This is due to higher content of alumina (30.8%) in metakaolin than that in OPC cement (4.9%). Figure 4.1 also shows that the accumulated released hydration heat per gram of 20% metakaolin blended cement at 72 h was improved up to 5% by the pre-carbonation method with 3% slaked lime, which is lower than the increase achieved by using pure cement. This is not surprising because the particle size of metakaolin is about 1 μm which is much smaller than cement (12 μm). Hence, the metakaolin itself can serve as nucleation sites for

hydration of cement, which makes the extra seeding sites provided by the produced CaCO_3 less pronounced.

Similarly, the cement paste produced with carbonated 3% slaked lime slurry exhibits a shorter dormant stage, especially compared to the control group. This is because 3% slaked lime slurry couldn't be fully carbonated using the present CO_2 bubbling method with the given carbonation duration. As a result, there should be some un-carbonated slaked lime existing in the pre-carbonated slurry, which can accelerate the hydration of cement.

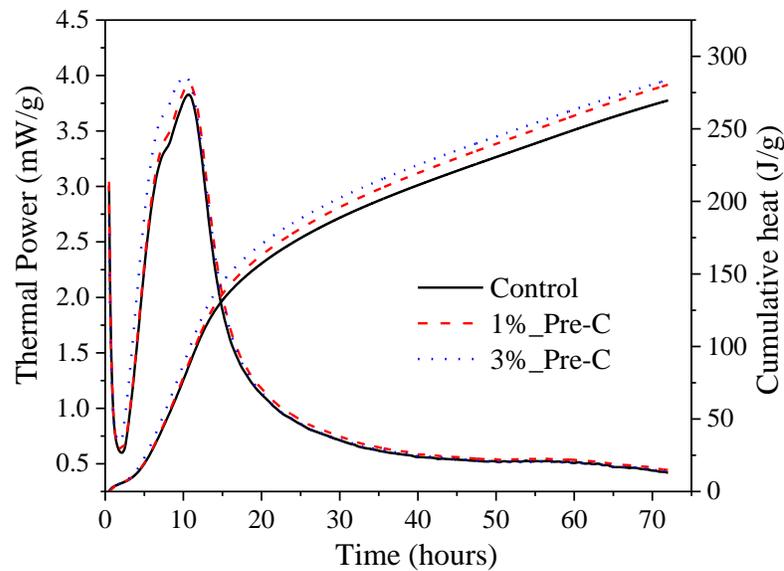


Figure 4.1. Isothermal calorimetry curves of metakaolin blended cement pastes produced with and without using pre-carbonation method

4.3.1.2 Effect of Pre-carbonation on Hydration Heat of fly ash blended OPC

The calorimetry tests were carried out on the fly ash blended cement pastes produced with and without using pre-carbonation method, as shown in Figure 4.2. The pre-carbonation group was produced by carbonating 1% slaked lime slurry at 23 °C for 10 min before mixed with fly ash blended cement. It can be seen that the pre-carbonation method clearly promotes the

hydration of fly ash blended cement paste. About 5% more accumulated hydration energy was achieved by the pre-carbonation method at 72 h.

Compared to pure cement, the hydration kinetics of the blended cement paste is greatly influenced by the replacement of fly ash. Both the control and pre-carbonated group exhibit a much longer dormant stage. The C_3A peak reached its maximum at 20 h compared to 8 h in the case of pure cement. This delay was also observed in other studies with fly ash blended cement due to the dilution effect. The delay caused by bicarbonate from pre-carbonation method, however, is diminished. The shape of the calorimetry curve has only one peak and is more likely belong to both C_3A and C_3S , which is significantly different from that of the pure cement paste or metakaolin blended cement paste.

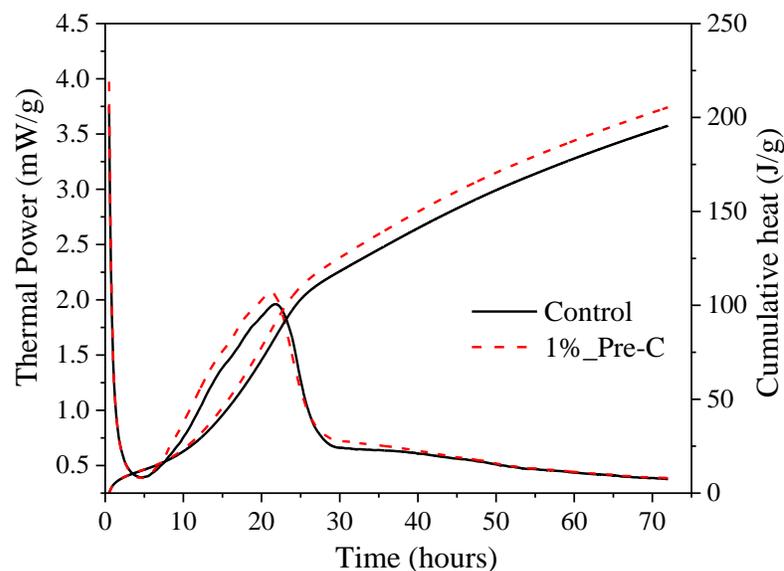


Figure 4.2. Isothermal calorimetry curves of fly ash blended cement pastes produced with and without using pre-carbonation method

4.3.2 XRD

XRD analyses were carried out to study the hydration product of metakaolin blended cement paste produced by carbonating 1% and 3% slaked lime at 23 °C for 10 min and 15 min,

respectively. The XRD patterns of metakaolin blended cement paste at 4 d are presented in Figure 4.3. It can be seen that significant amount of ettringite exists in all samples, which is much more than that in the pure OPC-based paste. More ettringite was produced in the pre-carbonated groups. This is because the aluminum from metakaolin helps produce more ettringite, and the presence of CaCO_3 produced by pre-carbonation can stabilize it [135]. The peaks for different phases of AFm were not detected in this study, either.

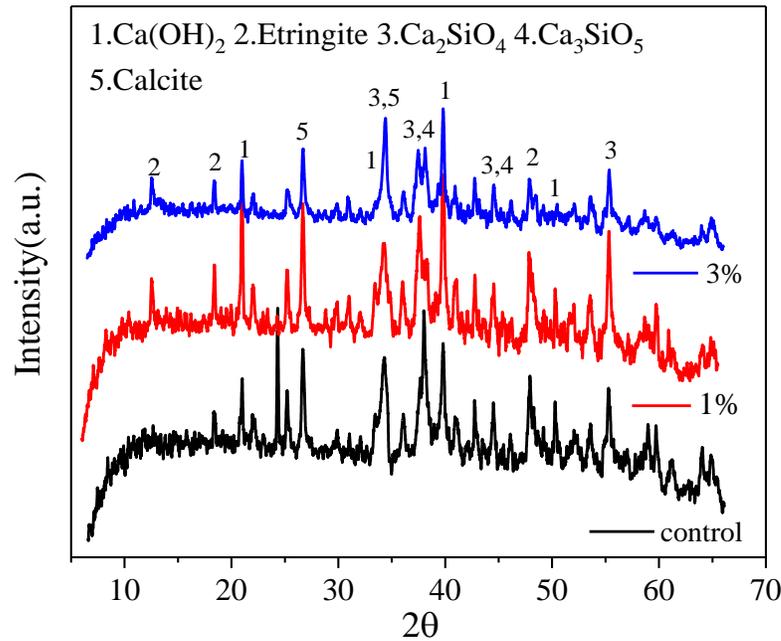


Figure 4.3. XRD patterns of metakaolin blended cement pastes produced with and without using pre-carbonation method

4.3.3 Thermogravimetric Analysis

Figure 4.4 shows the TGA results of metakaolin blended paste prepared with/without using pre-carbonation method at 4 d. The pre-carbonated cement pastes were produced by carbonating 1% and 3% slaked lime at 23 °C for 15 min and 20 min, respectively. The derivative of mass loss is also presented in Figure 4.4.

The calculated weight losses of ettringite, AFm, portlandite and calcite are presented in Table 4.4 based on the temperature range mentioned in Section 3.3.4. Similar to the case of pure

cement paste examined in Chapter 3, more ettringite was found in all pre-carbonated samples, which is in good agreement with the XRD results shown in Figure 4.3. Among these three groups, the one produced by pre-carbonating 3% slaked lime has the lowest content of CH. This is because more CH was consumed by the pozzolanic reaction between CH and metakaolin in this sample than in others, which is in agreement with the calorimetry results, where 3% group had strongest peak of C_3A . The amount of calcite in the 1% group is lower than the control one, probably due to the formation of monocarbonate or hemicarbonate phases. No significant difference with respect to the content of AFm (including both monocarbonate and monosulfate) was found among these samples.

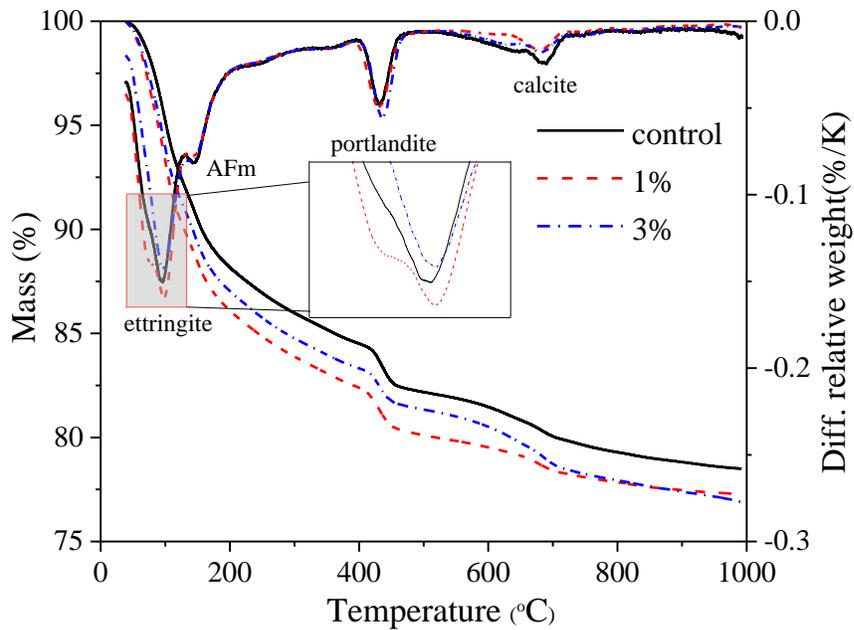


Figure 4.4. TGA results of metakaolin blended cement pastes produced with and without using pre-carbonation method at 4 d

Table 4.4. The calculated weight losses of metakaolin blended cement pastes at 4 d

Specimen	Weight loss (%) related to the decomposition of			
	Ettringite	AFm	CH	Calcite
Control	3.34	0.65	2.33	0.84
1%	3.78	0.64	2.30	0.69
3%	3.58	0.65	2.0	0.93

4.3.4 Mechanical Properties

Calorimeter results suggest that the hydration of metakaolin/fly ash blended cement is promoted by the pre-carbonation method. The mechanical properties of metakaolin/fly ash blended cement mortars are expected to be enhanced by the pre-carbonation method.

4.3.4.1 Compressive Strength

4.3.4.1.1 Metakaolin Blended Cement Mortar

Figure 4.5 shows the compressive strengths of metakaolin blended cement mortars with 1% and 3% slaked lime slurry pre-carbonated at 23 °C. The compressive strengths of the mortar samples with pre-carbonated 3% slaked lime were enhanced by 21%, 19% and 13%, at ages of 3, 7, 28 d, respectively. With pre-carbonated 1% slaked lime slurry, the compressive strength of the mortar was improved by 16%, 16% and 7%, at ages of 3, 7, 28 d, respectively. This suggests that more pre-carbonated slaked lime provides more seeding sites for the hydration of the cement. The workability, however, was reduced with the increased concentration of the slaked lime. Therefore, superplasticizer was added to the fresh cement mortar to achieve the same workability for all control and pre-carbonation groups.

Figure 4.5 also shows that more improvement on compressive strength can be achieved by pre-carbonation method for the metakaolin blended cement mortars than the pure cement mortars examined in Chapter 3 with pre-carbonated 1% and 3% slaked lime slurry. This difference may be attributed to that more ettringite was produced and stabilized by pre-carbonation in the metakaolin blended cement mortar than in the pure cement mortar, as confirmed by the TGA and XRD result shown in Figures 4.3 and 4.4.

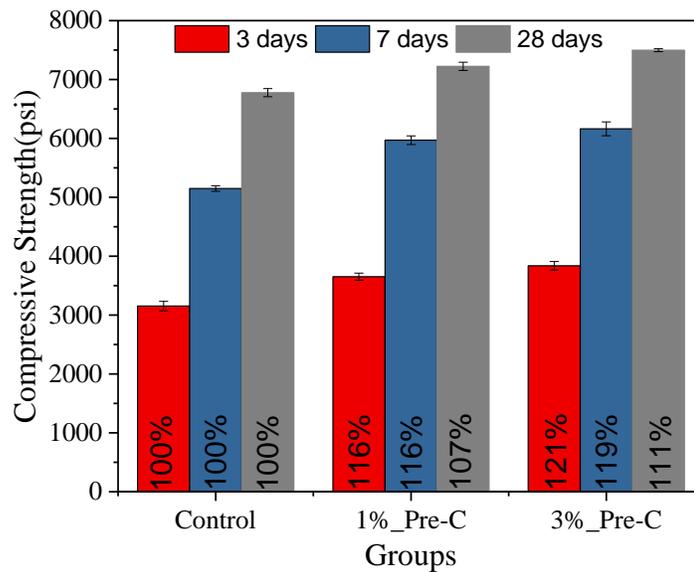


Figure 4.5. Compressive strengths of metakaolin blended cement mortars produced with and without using pre-carbonation method

4.3.4.1.2 Fly Ash Blended Cement Mortar

Figure 4.6 compares the compressive strength of fly ash blended cement mortars prepared with and without using the pre-carbonation method. It can be seen that the compressive strength of this mortar is improved by the pre-carbonation regardless the concentration of the slaked lime slurry. Similar to the case of metakaolin blended cement mortar, more pronounced strength improved was achieved by the mortar with pre-carbonated 3% slaked lime slurry. In this case, pre-carbonation didn't induce workability loss to the mortar due to the 30% replacement cement

with fly ash. The compressive strengths of all fly ash blended cement mortars, however, are greatly reduced compared to the pure cement mortar due to the slow rate of the pozzolanic reaction between the fly ash and CH in the mortar.

In addition to extra nucleation sites induced by the pre-carbonation method, the presence of CaCO_3 also helps produce more hemihydrate/monohydrate in fly ash blended cement mix compared to pure cement mix [143] due to a lower $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio. This can also benefit the strength development of mortars.

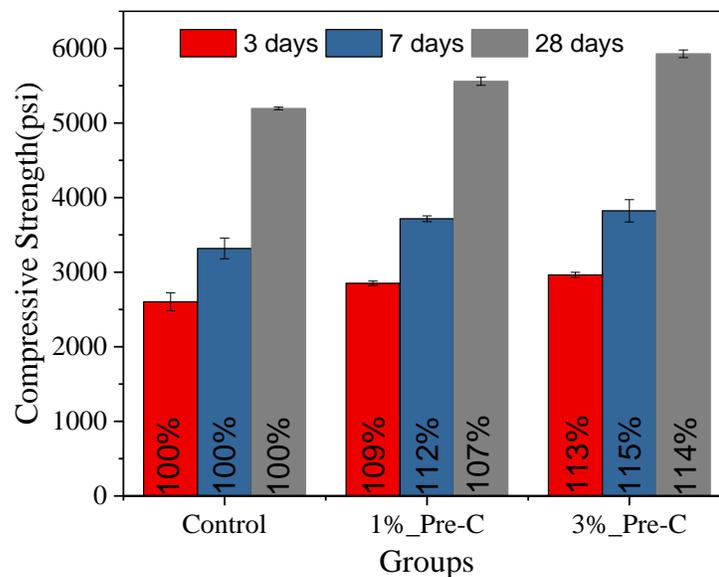


Figure 4.6. Compressive strengths of fly ash blended cement mortars produced with and without using pre-carbonation method

4.3.4.2 Flexural Strength

Figure 4.7 compares the flexural strengths of control mortar and the ones produced through pre-carbonating 1% slaked lime slurry at 23 °C at 7 and 28 d, respectively. By using the pre-carbonated method, the flexural strength of the metakaolin blended cement mortar was enhanced by 9% and 10% at 7 and 28 d, respectively. The flexural strength of the fly ash blended cement mortar was enhanced by 4% and 5% at 7 and 28 d, respectively. Similar to compressive strength,

this improvement on the flexural strength of the metakaolin/fly ash mortars is mostly due to the promotion effect of the pre-carbonation on the hydration of the cement.

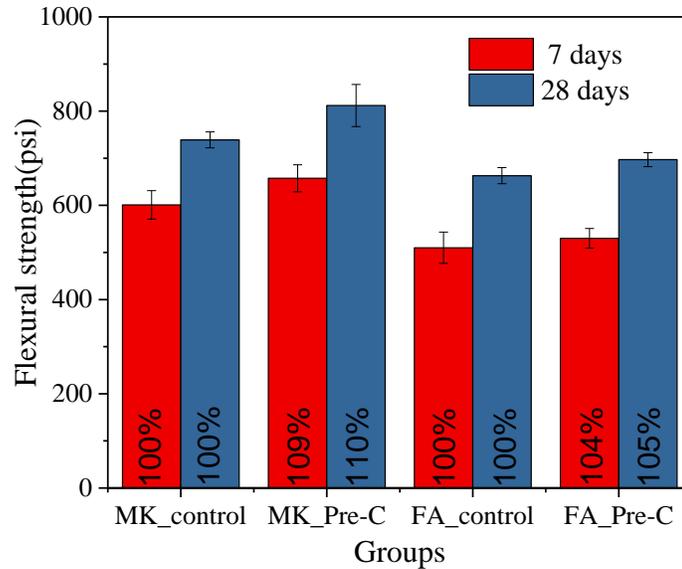


Figure 4.7. Flexural strengths of metakaolin/fly ash blended cement mortars produced with and without using pre-carbonation method

4.3.5 Durability

The durability tests, including water absorption test and sulfate resistance test, were carried out on the metakaolin blended cement mortar using pre-carbonation method. As compared to the pure cement mortar, more ettringite was produced in the blended cement mortar due to extra alumina from metakaolin. Hence, the total volume of the hydrated phases in this mortar can be higher than that in the pure cement mortar, leading to a lower porosity in the blended cement mortar. Since the pre-carbonation method can help stabilize the ettringite in the mortar, it can improve the durability of metakaolin blended cement paste.

4.3.5.1 Water Absorption Test

Figure 4.8 shows the rate of water absorption of metakaolin blended cement mortars: one control mortar and one pre-carbonated mortar produced by carbonating 3% slaked lime slurry.

As compared to the control group, the pre-carbonated group exhibits lower water absorption rate from 0.25 h to 24 h. Water absorption at 24 h was reduced by 5% by the pre-carbonation method. It should be mentioned that the workabilities of both groups were adjusted to the same level by using superplasticizer. Hence, if no workability loss occurs, pre-carbonation method can clearly reduce the permeability of the mortar. As discussed in Chapter 3, this improvement on the water absorption of the mortar samples is presumably due to the denser microstructure induced by the pre-carbonation. The overall water absorption of the metakaolin blended cement mortar is lower than that of the pure cement mortar due to better packing between cement and metakaolin particles.

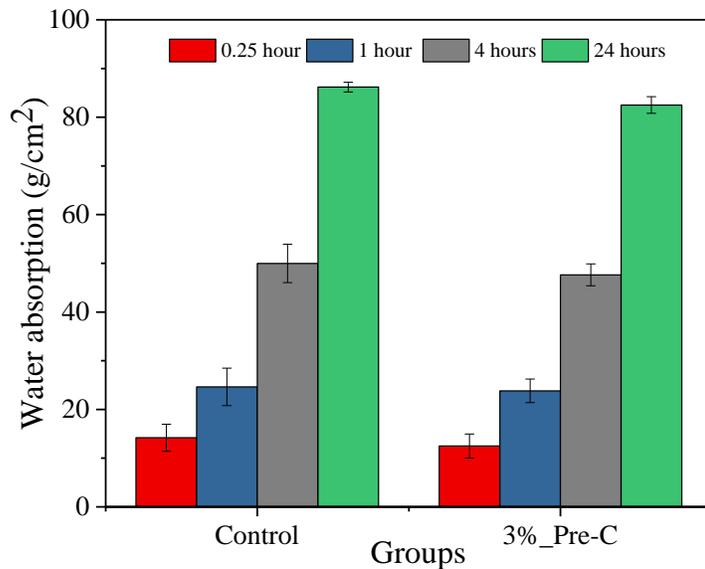


Figure 4.8. Water absorption of metakaolin blended cement mortars produced with and without using pre-carbonation method

4.3.5.2 Sulfate Resistance Test

Figure 4.9 shows the expansion of metakaolin blended cement mortar bars immersed in 50 g/L sulfate solution. As compared to the control group, the expansion of the mortar bars was effectively reduced by the pre-carboantion method. It can be seen that the expansion of the pre-

carbonated mortar with 3% slaked lime is lower than that of the control one, suggesting that pre-carbonating 3% slaked lime can improve the sulfate resistance of the mortar. In Chapter 3, the poor workability of the mortar leads to a higher permeability of the pre-carbonated sample with 3% slaked lime slurry, which is compensated by the addition of superplasticizer in this mortar.

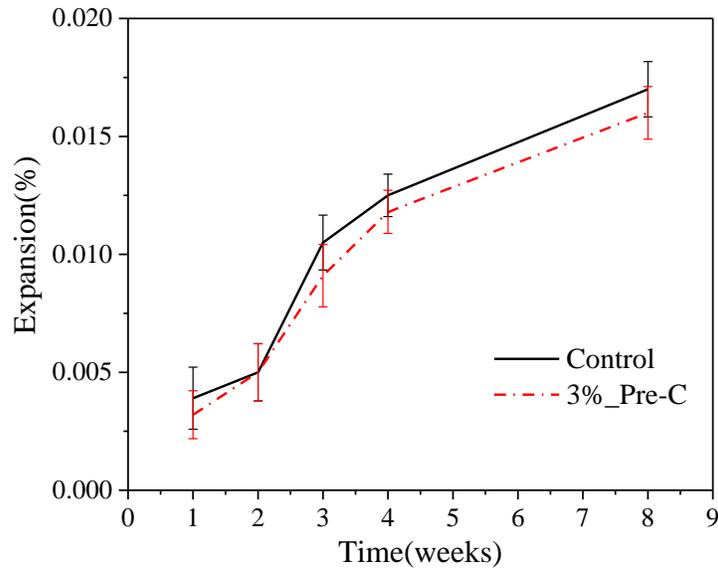


Figure 4.9. Expansions of metakaolin blended cement mortars produced with and without using pre-carbonation method in 50/L sodium sulfate solution.

4.4 Conclusions

In this chapter, the effects of pre-carbonation method on the behaviors of metakaolin/fly ash blended mortars were examined. Experimental studies showed that both mechanical properties and durability can be improved by the pre-carbonation method. A few conclusions can be drawn based on the studies carried out in this chapter as follow:

- Hydration of metakaolin/fly ash blended cement can be promoted by using the pre-carbonation method.

- TGA and XRD results showed that pre-carbonation does change the mineralogy of the hydrated metakaolin blended cement. More ettringite was found in the samples produced by the pre-carbonation method.
- The compressive and flexural strengths of both fly ash and metakaolin blended cement mortars were improved by the pre-carbonation method. More improvement on compressive strength can be achieved by the mortar using higher concentrated slaked lime with same workability.
- The pre-carbonation method is more effective with metakaolin blended cement mortars.
- Based on water absorption and sulfate resistance tests, the durability of metakaolin blended cement mortar can be improved by the pre-carbonation method.

CHAPTER 5

ALTERNATIVE CALCIUM SOURCES FOR PRE-CARBONATION

5.1 Introduction

Although slaked lime has been successfully used as calcium source to produce CaCO_3 nanoparticles in fresh concrete using the pre-carbonation method, its production releases significant amount of CO_2 emission. Many other calcium-rich minerals can also be used as the calcium source in the pre-carbonation method, such as Class C (high calcium) fly ash, ground granulated blast-furnace slag (GGFBS), and even cement itself. Since Class C fly ash and GGFBS are by-products from other industries, their production doesn't produce extra CO_2 emission. In this sense, it may be advantageous to use them in the pre-carbonation method. In this chapter, a preliminary study on other calcium-rich minerals to in-situ produce CaCO_3 nanoparticles in fresh cement mix with the pre-carbonation method is presented.

5.2. Other Calcium Source for Carbonation

5.2.1 Class C Fly Ash

The Class C fly ash was produced in James H. Miller, Jr. Electric Generating Plant (owned by Alabama Power/Southern Company), which has 26% calcium, as shown in Table 4.1.

5.2.1.1 Sample Preparation

To pre-carbonate the fly ash, the fly ash was first dissolved in the deionized water and mixed for 5 min using a magnet stir. The produced fly ash slurry was then carbonated at 7 °C for 15 min before mixed with cement.

For calorimetry and strength tests, 20% of the cement was replaced by the Class C fly ash. The fly ash was pre-carbonated before mixing with other ingredients of the mortar for compressive strength test, as shown in Table 5.1. It should be mentioned that the mortar with pre-carbonated fly ash experienced serious loss of workability.

Table 5.1. Mix proportions for fly ash blended cement mortars produced with/without pre-carbonation method (lbs/yd³)

Constituent	Control	Pre-C
Cement	485.6	485.6
Fly ash	121.4	121.4
Water	303.5	303.5
River Sand	1530.0	1530.0
Pre-Carbonation	-	Yes

5.2.1.2 Results and Discussions

Figure 5.1 shows the calorimetry results of the fly ash blended cement paste produced with and without using the pre-carbonation method. As discussed in Chapter 3, pre-carbonation at lower temperature (7 °C) can lead to a longer dormant period. This can be attributed to more Ca(HCO₃)₂ produced by carbonating the slaked lime slurry at the lower temperature because more CO₂ can be dissolved in water at a lower temperature. Nonetheless, it is expected that the accumulated energy released from the paste produced with pre-carbonated fly ash surpasses the control group in later ages due to a thinner diffusion barrier on the surface of the clinker.

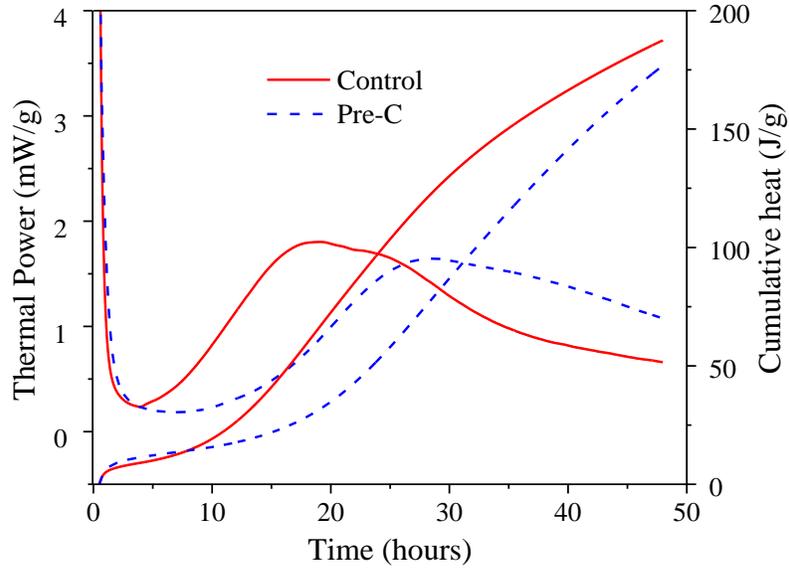


Figure 5.1. Isothermal calorimetry curves of cement pastes produced with and without using directly carbonation on fly ash

Figure 5.2 shows that pre-carbonated fly ash can enhance the compressive strength of the mortars by 18%, 6%, and 10% at ages of 3, 7, and 56 d, respectively. The speculation of calorimetry study is confirmed by this strength enhancement. This is only a preliminary result with 15 min pre-carbonation. The compressive strength of the group with pre-carbonated fly ash, exhibited larger variation, due to the poor workability of the fresh mortar. Further study is needed to find out the potential of fly ash as calcium source for pre-carbonation method.

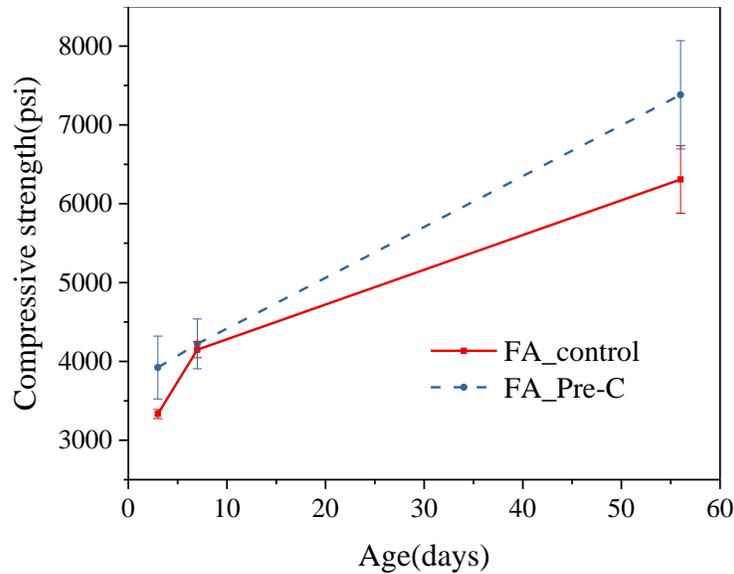


Figure 5.2 Effect of Pre-carbonation method on the compressive strengths of fly ash blended mortars

5.2.2 Limestone

As shown in Equation 2.4, excessive carbonation of CaCO_3 can produce bicarbonate, which can react with Ca(OH)_2 in fresh concrete to produce CaCO_3 nanoparticles. For this reason, limestone was also examined as the calcium source in the pre-carbonation method.

5.2.2.1 Sample Preparation

The limestone powders (94% calcite), which is used to partially replace cement, were first mixed in water for 5 min using a magnet stir. Then the produced limestone slurry was carbonated for 15 min at 7 °C and then mixed with cement. Three groups of samples were made to evaluate the effect of pre-carbonating the limestone powders on the compressive strength of the mortars, as shown in Table 5.2. The control group was made by replacing 20% of cement with the limestone powders. Two pre-carbonated groups were made to evaluate the effect of pre-carbonation method. The Pre-C group was made using the same mix as the control group. However, the limestone powders used in this mortar were first mixed with water to produce the limestone slurry which was then carbonated by bubbling CO_2 in the same way as the slaked lime

slurry was carbonated. Then the slurry was mixed with cement to produce the Pre-C mortar. The 1%_Pre-C group was made by replacing 20% of cement with limestone powders and 1% pre-carbonated slaked lime slurry.

Table 5.2 Mix proportions for limestone blended cement mortars produced with/without using pre-carbonation method (lbs/yd³)

Constituent	Control	1%_Pre-C	Pre-C
Cement	485.6	483.2	485.6
Limestone	121.4	120.8	121.4
Water	303.5	303.5	303.5
River Sand	1530.0	1530.0	1530.0
Slaked Lime	-	3.0	-
Pre-Carbonation	-	Yes	Yes

5.2.2.2 Results and Discussion

Figure 5.3 compares the compressive strength of limestone blended cement mortar made with and without using the pre-carbonation method. Compared with the control group, the Pre-C group has slightly higher compressive strength at ages of 3, 7, and 28 d, as shown in Figure 5.3. This improvement induced by simply carbonating the limestone powders can be attributed to the bicarbonates in the carbonated limestone slurry produced by the CO₂ bubbling. As discussed before, these bicarbonates can react with Ca(OH)₂ in the mortar to in-situ produce CaCO₃ nanoparticles in the fresh mortar, which promote the hydration of the cement, leading to higher compressive strength at all ages. Due to the low concentration of bicarbonate in water in ambient environment, the produced CaCO₃ nanoparticles are very limited, resulted in a slight strength improvement of the produced mortar. In this sense, limestone powders are not an ideal calcium source for the pre-carbonation method.

Much higher strength improvement was achieved by the 1%_Pre-C group. As shown in Figure 5.3, the compressive strength of this mortar was improved by 17%, 13%, and 19% at 3, 7, and 28 d, respectively. This enhancement is resulted from the in-situ produced nanoparticles by carbonating the slaked lime slurry, which promotes the hydration of the cement.

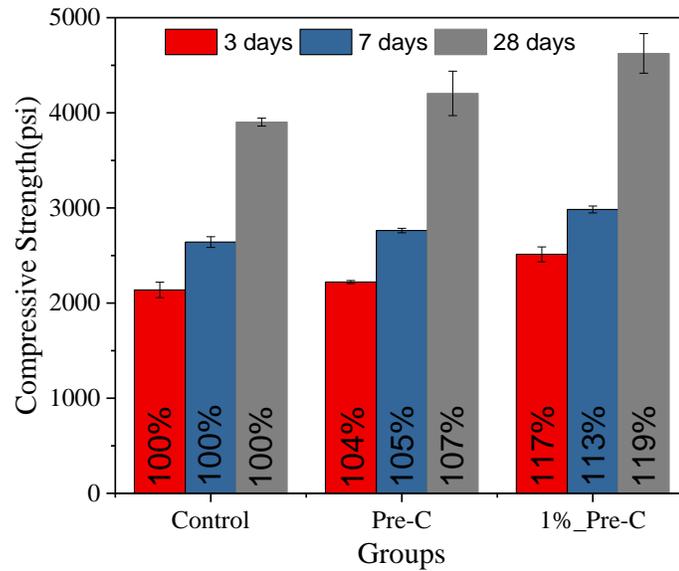


Figure 5.3. Effect of Pre-carbonation method on the compressive strengths of limestone blended mortars

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

In this dissertation, a novel technique – pre-carbonation method – was proposed to improve the strength and durability of OPC-based mortar/concrete. A comprehensive experimental program on the underneath mechanisms and application potential of the pre-carbonation method has been carried and presented in this dissertation. The slaked lime slurry carbonated under various conditions was first characterized, which provides insight to the working mechanism of the pre-carbonation method. Then a series of experimental studies were carried out to evaluate the effects of the pre-carbonation method on the performances of cement based mortars/concretes. Two major working mechanisms of the pre-carbonation method were proposed by correlating the carbonation products in the carbonated slaked lime slurry to the performance of the produced cement mortar/concrete:

- 1) Carbonating the calcium-rich slurry in-situ produces CaCO_3 nanoparticles in the mix of mortar/concrete. Their high surface area provides extra seeding sites for the hydration products of the cement, significantly promoting the hydration of the cement.
- 2) The carbonate produced by the pre-carbonation tune the mineralogy of the hydrated cement. More ettringite is produced in the pre-carbonated samples, leading to a denser microstructure with lower porosity due to increased volume of the hydrated phases.

This new technique was also successfully extended to an environmentally friendly construction materials, blended cement based mortar in which supplementary cementitious materials such as fly ash and metakaolin were used to partially replace OPC. Some conclusions can be drawn based on the work carried out in this dissertation research.

6.1.1 Carbonation Conditions and Carbonation Products in The Slaked Lime Slurry

- Four factors affect the particle size or morphology of the produced CaCO_3 precipitate in the carbonated slaked lime slurry: carbonation duration, carbonation temperature, slaked lime concentration, and dispersion method.
- The particle size of the CaCO_3 precipitate is dependent on all factors mentioned above. Shorter carbonation duration, lower carbonation temperature, and lower slaked lime concentration are desirable to produce smaller size of CaCO_3 . Sonicating is more effective than magnetically stirring the slurry to produce smaller CaCO_3 particles during the carbonation.
- The morphology of the CaCO_3 particles produced by carbonating the slaked lime slurry is affected by the concentration of the slurry.
- The average size of the CaCO_3 particles produced by carbonating 1% slaked lime is less than 130 nm and 157 nm at 7 °C and 23 °C, respectively, confirming that nanoparticles can be in-situ produced by the proposed pre-carbonation method. These particles provide heterogenous nucleation site for cement hydration.

6.1.2 Effect of Pre-Carbonation Method on The Performance of Cement Based Binder

6.1.2.1 Early Age Hydration

- Hydration of cement can be significantly promoted by the proposed pre-carbonation method. This improvement in hydration of cement can be attributed to high surface area of the CaCO_3

particles produced by carbonating the slaked lime slurry, which provide heterogenous nucleation sites for the hydration of cement. Higher surface area leads to higher rate of hydration.

- The presence of bicarbonate in the carbonated slaked lime slurry leads to formation of CaCO_3 nanoparticles in fresh mortar/concrete by reaction with $\text{Ca}(\text{OH})_2$. On one hand, this reaction consumes Ca^{2+} ions in fresh mortar/concrete, which can delay of the formation of hydration products of cement. On the other hand, the new nanoparticles produced by this reaction function as nucleating seeds for hydration products of the cement, and therefore, promotes the hydration of the cement and compensates the delay effect of this reaction.
- Hydration products of cement can be tuned by the pre-carbonation. More ettringite and less calcite were found in the mortar samples produced by the pre-carbonation method. The porosity of cement mortar produced by the pre-carbonation method is lower than the control group. This is because higher volume of hydration products can be produced in the pre-carbonated mortar due to the formation of more ettringite.

6.1.2.2 Long Term Behaviors of Mortars/Concretes

- Mechanical properties of mortar/concrete samples, including compressive strength, flexural strength, and modulus of elasticity can be enhanced by the pre-carbonation method, especially at early age. More improvement on long-term mechanical properties can be achieved by carbonating the slaked lime slurry at lower temperature.
- Permeability of cement mortar can be reduced by the pre-carbonation method. When high concentrated slaked lime slurry is used, the loss of workability after carbonating the slurry can lead to higher permeability. The sulfate resistance of the mortar is also improved by the

pre-carbonation method because ettringite is stabilized in the mortar by the CaCO_3 produced by carbonating the slaked lime slurry.

- The dry shrinkage of cement mortar can be slightly reduced by the pre-carbonation method at early age.
- The reduction of the pH value of the pore solution of the mortar induced by the pre-carbonation method is negligible.

6.1.3 Effect of Pre-Carbonation Method on The Performance of SCMs blended Cement Mortars

- The pre-carbonation method has been successfully extended to SCMs blended cement mortars. The compressive and flexural strengths of both fly ash and metakaolin blended cement mortars can be improved by the pre-carbonation method. Higher improvement was achieved by the metakaolin blended cement mortar.
- Higher content of ettringite can be induced into the hydration products of the metakaolin blended cement by the pre-carbonation method.
- The durability of metakaolin-based cement mortar is improved by the pre-carbonation method, mainly due to denser microstructure of the mortar induced by the promoted hydration of the cement and increased volume of hydrated phase.

6.2 General Guidelines for the Pre-Carbonation Method

Based on the research summarized above, general guidelines for applying pre-carbonation method can be summarized as follows:

- For pure cement based mortar/concrete, slaked lime can be used as calcium source for pre-carbonation. The concentration of the slaked lime slurry should be in the range between 1% to 3%. If higher slaked lime concentration is used, superplasticizer is suggested to use to adjust the workability.

- Pre-carbonation can work at both low and ambient temperatures. Lower carbonation temperature is beneficial to achieve a higher long-term strength.
- The best w/c ratio for applying the pre-carbonation method ranges from 0.4 to 0.6.
- For SCM blended cement mortar/concrete, pre-carbonation with slaked lime slurry is suggested. When calcium-rich SCMs like class C fly ash is used, the SCM itself can also serve as calcium source of pre-carbonation. However, there will be a substantial loss of workability at high replacement of the cement and superplasticizer should be added.
- Ultrasonication is the preferred dispersion method compared to magnet stirrer. Sonication can help disperse the nanoparticles produced using pre-carbonation method more homogenously.

6.3 Future Work

This dissertation research demonstrates that pre-carbonation can improve the strength and durability of cement-based mortar/concrete. The underneath mechanisms of the pre-carbonation methods have also been examined. Since the pre-carbonation method is a brand-new technology, more study should be carried out in the future to further optimize this method so that better enhancement on the performance of mortar/concrete can be achieved. Some future work is listed below:

- Calcium-rich minerals as by-products of other industries should be examined to replace slaked lime as calcium source for the proposed pre-carbonation method. One objective of this dissertation research is to reduce the carbon footprint of concrete. Since slaked lime is produced by driving CO₂ out of limestone, carbonating the slaked lime only re-absorbs those released CO₂ back into the concrete. By using calcium-rich by-products of other

industries such as high calcium fly ash, GGFBS, extra CO₂ can be absorbed into the produced mortar/concrete.

- Pure CO₂ gas was used in this study to carbonate the calcium-rich minerals. It is envisioned that flue gas from power plant or cement plant should be used in pre-carbonation technique. Therefore, future study should be carried out to examine whether similar effects can be achieved by using the flue gas to carbonate the calcium sources.
- Further research is needed to accurately quantify the content of monosulfate and monocarbonate in the mortar/concrete produced by the pre-carbonation method. The instrument used in this study failed to capture these 2 AFm phases on the measured XRD patterns. However, their contents in the mortar/concrete is critical to understand the mechanism of the pre-carbonation method on modifying the hydrate phases of the cement.
- More work should be carried out to standardize the carbonation process. For example, the pressure of the CO₂ gas can also play an important role in carbonating the calcium source slurry. However, the testing set-up used in this study does not provide reliable control over the pressure of the CO₂ gas, and therefore, its effect on the carbonation result has not been examined yet.

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