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INDIANA DEPARTMENT OF TRANSPORTATION
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Performance of Portland Limestone Cements: Cements Designed to Be More Sustainable That Include up to 15% Limestone Addition



Timothy J. Barrett

Hongfang Sun

W. Jason Weiss

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AUTHORS

Timothy J. Barrett

Graduate Research Assistant
Lyles School of Civil Engineering
Purdue University

Hongfang Sun

Graduate Research Assistant
Lyles School of Civil Engineering
Purdue University

W. Jason Weiss, PhD

Jack and Kay Hockema Professor of Civil Engineering
Director of the Pankow Materials Laboratory
Lyles School of Civil Engineering
Purdue University
(765) 494-2215
wjweiss@purdue.edu
Corresponding Author

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JOINT TRANSPORTATION RESEARCH PROGRAM

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16. Abstract <p>In 2009, ASTM and AASHTO permitted the use of up to 5% interground limestone in ordinary portland cement (OPC) as a part of ASTM C150/AASHTO M85. When this project was initiated a new proposal was being discussed that would enable up to 15% interground limestone to be considered in ASTM C595/AASHTO M234 cement. This project was initiated to provide rapid feedback to INDOT for use in discussions regarding these specifications (this has become ASTM C595/AASHTO M234). PLC is designed to enable more sustainable construction which may significantly reduce the CO₂ that is embodied in the built infrastructure while extending the life of cement quarries. The physical and chemical properties of the cementitious materials used in this study were examined. PLC is typically a finer cement (10 to 30% Blaine fineness) with a reduction in the coarse clinker particles (>20µm) and an increase in fine particles which are primarily limestone. Isothermal calorimetry and chemical shrinkage results imply that these PLC materials have a similar or slight greater reaction and would be able to be used interchangeably with OPC in practice as it relates to the rate of reaction. The PLC mortars exhibited relatively similar activation energies compared to the corresponding OPCs allowing the maturity method to be used by INDOT for both the PLC and OPC systems. The mechanical properties of OPC and PLC were generally similar with the PLC typically having slightly higher early age strengths but similar 28 day strengths. No significant change in drying shrinkage or restrained shrinkage cracking was observed for the PLC when compared with OPC (Barrett et al. 2013). The PLC has similar volumes of permeable voids as the OPC. The chloride diffusion coefficients in the PLC systems may range from 0 to 30% higher than the OPCs. The PLC showed synergistic benefits when paired with fly ash. Based on the available literature and available testing results INDOT could consider PLC, as specified in accordance with ASTM C-595/AASHTO M 240, to be a suitable option for use in INDOT concrete applications.</p>		13. Type of Report and Period Covered Final Report	
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EXECUTIVE SUMMARY

PERFORMANCE OF PORTLAND LIMESTONE CEMENTS: CEMENTS DESIGNED TO BE MORE SUSTAINABLE THAT INCLUDE UP TO 15% LIMESTONE ADDITION

Introduction

In 2009, ASTM and AASHTO permitted the use of up to 5% interground limestone in ordinary portland cement (OPC) as a part of ASTM C150/AASHTO M85. When this project was initiated, a new proposal was being discussed that would enable up to 15% interground limestone to be considered in ASTM C595/AASHTO M240 cement. This project was initiated to provide rapid feedback to INDOT for use in discussions regarding these specifications. This information was provided during the project and this report documents those findings.

The proposal for increasing the volume of limestone that would be permitted to be interground in ASTM C595/AASHTO M240 cement is designed to enable more sustainable construction which may significantly reduce the CO₂ that is embodied in the built infrastructure while extending the life of cement quarries. Further, as Indiana is a large producer of limestone based products it may be possible to use limestone as a part of the binder and not just a filler. This could alter both environmental and economic considerations for the concrete in transportation structures for use in paving (Figure 1) or transportation structure applications.

Significant research regarding the properties with interground limestone has been conducted by the cement industry since these cements became widely used in Europe over three decades ago. Recently, two main reviews of this work have been developed for application in North America.¹ Based on these reviews, it was determined that further studies be performed to understand how low temperature sulfate attack can occur and to understand the impact of exposure to high concentrations of deicing salts on joint deterioration. Research to address the concern of sulfate attack is



Figure 1 Typical PCCP paving.

¹Hooton, R., M. Nokken, M., and M. Thomas. *Portland-Limestone Cement: State-of-the-Art Report and Gap Analysis for CSA A3000*. Cement Association of Canada, Ottawa, Ontario, Canada, 2007; Tennis, P. D., M. D. A. Thomas, and W. J. Weiss. *State-of-the-Art Report on Use of Limestone in Cements at Levels of up to 15%*. Portland Cement Association, Skokie, Illinois, 2011.

being performed under the direction of Hooton at Toronto and Thomas at New Brunswick. Research to address the potential impact of exposure to high concentrations of deicing salts is ongoing at Purdue University. The present work focuses on North American PLCs, designed to be equivalent replacements for OPC, and performs a series of tests that will be of interest in terms of early age and standard DOT tests.

Findings

The physical and chemical properties of the cementitious materials used in this study were examined. Intergrinding the limestone with portland cement clinker (to make PLC that is consistent with ASTM C595/AASHTO M240) is primarily a physical process that does not appear to result in any chemical alterations of the portland cement clinker. Intergrinding the limestone with the clinker results in a finer powder with a reduction in the coarse clinker particles (>20 μ m) and an increase in fine particles which are primarily limestone. The specific surface area (Blaine fineness) of the PLC increased by 10% to 30% in comparison to the corresponding OPC to reduce the effects of dilution. SEM images were captured and showed that for the PLC system the limestone is ground finer than the cement.

The hydration reaction each material was assessed to evaluate the effects of including limestone particles in cementitious systems. Generally the PLC mortars exhibited a slightly greater heat release than the OPC (i.e., greater hydration reaction) after 7 days. Calorimetry and chemical shrinkage results indicate that these PLC materials would be able to be used interchangeably with OPC in practice as it relates to the rate of reaction. In addition, the PLC mortars exhibited similar activation energies compared to the corresponding OPCs. This would allow the maturity method to be used by INDOT for both the PLC and OPC systems.

The mechanical properties of OPC and PLC were assessed to determine the time of set, the modulus of elasticity, compressive strength, flexural strength, drying shrinkage, and restrained autogenous shrinkage. The time of set for the PLCs was on average 10% earlier than OPCs. Generally, the PLCs show an increase in compressive strength at early ages that diminishes with time, resulting in similar compressive strengths at 28 days of age. In general the elastic modulus and flexural strength of the OPC and PLC systems were similar (Figure 2).

No significant change in drying shrinkage or restrained shrinkage cracking was observed for the PLC 2 when compared with OPC (Figure 3).²

The transport properties tested include the chloride diffusion coefficients, the bulk electrical resistivity, and the rate of water absorption. The chloride diffusion coefficients from the migration cell testing showed that while the PLC have similar volumes of permeable voids as their OPC counterparts, the chloride diffusion coefficients in these systems may range from 0% to 30% higher than the OPCs. The results from the migration cell testing indicated that both cementitious systems (OPC and PLC) containing fly ash have chloride diffusion coefficients that are up to 90% lower than the same systems without fly ash.

The initial and secondary rates of absorption for the PLCs varied within $\pm 30\%$ of the reference OPCs, while the blended limestone systems showed an average increase of up to 30%

²Barrett, T. J., H. Sun, C. Villiani, L. Barcello, and W. J. Weiss. Early-Age Shrinkage Behavior of Portland Limestone Cement. *Concrete International*, Vol. 36, No. 2, 2014.

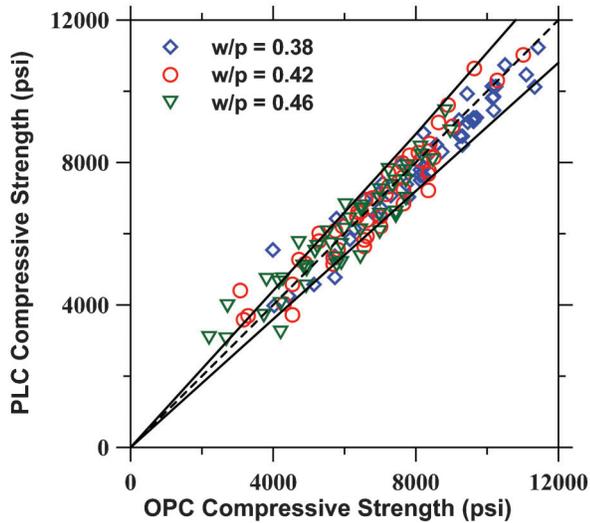


Figure 2 PLC compressive strength plotted versus each mixture's reference OPC. The dashed line indicates a 1:1 relationship, while the solid lines indicate $\pm 10\%$.

compared to their reference. Both the OPC and PLC have a similar degree of saturation while literature has shown similar freeze-thaw resistance when these materials are used in properly air entrained mixtures.

Implementation

Based on a review of the literature and the experiments performed in this research the following suggestions are provided for implementation.

- INDOT may consider PLC, as specified in accordance with ASTM C595/AASHTO M240, to be a suitable option for use in INDOT concrete applications.
- Ongoing research is being conducted to assess potential performance in high sulfate concentrations or in the presence of concentrated deicing salts which INDOT should monitor. Unless something negative is observed from the sulfate or deicing salt studies, PLC conforming to ASTM C 595, AASHTO M240 should be able to be used interchangeably with OPC.
- An educational module will be developed for the 2014 road school and subsequent use that introduces PLC materials to potential users. The educational module will enable INDOT personnel and INDOT contractors better understand what PLCs are and how they behave.
- INDOT is well positioned to consider using PLC on large scale paving field trials. INDOT should work with the local cement industry to identify projects that may have the potential to utilize the PLC on a coming project. The field performance of the PLC should be monitored and if the results are favorable this would provide INDOT with additional material options for paving.

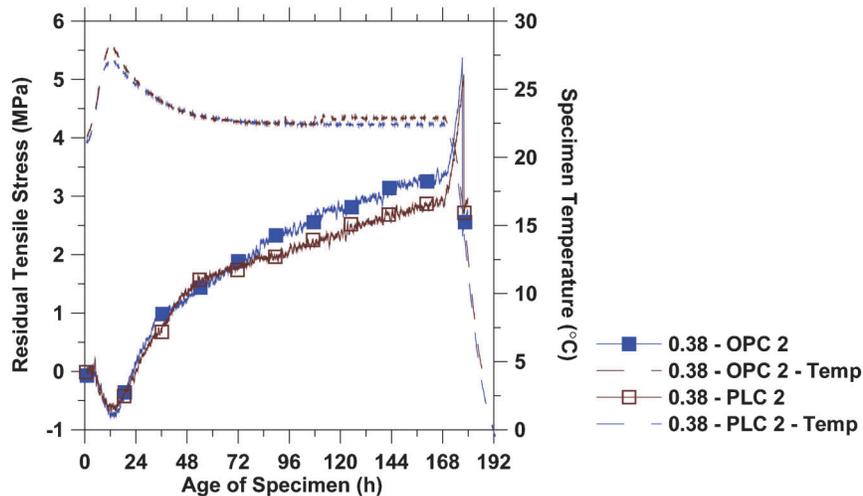


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1. INTRODUCTION

1.1 Background and Problem Statement

The Environmental Protection Agency (EPA) has proposed new regulations targeting a reduction of greenhouse gas emissions (especially CO₂) from the manufacturing process of ordinary portland cement (OPC). To address the required emission reductions, the cement industry is focusing on reducing clinker contents by intergrinding materials like limestone, slag, or fly ash during the grinding process of cement clinker. Recently, ASTM and AASHTO have permitted the use of up to 5% interground limestone in ASTM C150 cements (1). At the time this project started, a proposal was put forth to enable the use of up to 15% of interground limestone. This proposal was being reviewed by the state DOTs for potential adoption and information was needed regarding the performance of commercial portland limestone cement (PLC) made using different clinker with their corresponding OPC. A summary of research on PLC was presented to AASHTO and ASTM. This proposal resulted in a change in the ASTM C 595 and AASHTO M240 specifications to incorporate up to 15% of interground limestone. By increasing the volume of limestone that is interground with the clinker, significant reductions in CO₂ in the built infrastructure (i.e., reductions in clinker content) will be realized. In addition, this process can also further extend the life of cement quarries.

Significant research regarding the properties and durability of concrete with interground limestone (known in the rest of the document as portland limestone cement) has been conducted by the cement industry (2). Recently, two main reviews of this work have been developed to assess its application in North America. Hooton et al. (3) developed a state-of-the-art report for the Portland Cement Association of Canada discussing research on portland cement containing limestone that has taken place around the world. This report also identified where additional research is needed for application in North America. Based on that study, it was determined that further studies be performed regarding low temperature sulfate attack. Studies on low temperature sulfate attack are underway in Canada under the direction of Professors Doug Hooton at Toronto and Michael Thomas at New Brunswick. Further, it was recommended that potential interaction with deicers be studied given the potential for scaling or joint deterioration. This work is currently being conducted at Purdue University under the direction of Professor Jason Weiss. Tennis et al. (4) developed a state-of-the-art document with complete references specifically outlining items for discussion at ASTM and AASHTO as modifications to specifications were discussed. The document by Tennis et al. specifically highlighted the history of limestone cements, the benefits of using limestone, recent case studies, and the importance of limestone particle size and quality. The work shows that finer limestone, when

added separately, is beneficial for accelerating reactions, however there may be potential implication on volume change (i.e., shrinkage) (5). It should be noted that the studies by Bucher also considered interground limestone as well as limestone that may be blended with the cement as a fraction of binder. Bucher (6) showed that the separate addition of limestone can result in a reduction of properties (i.e., dilution) and this has also been observed by Neithalath et al (7).

In addition to these reviews, recent work (as a part of a FHWA funded study being conducted at Purdue with collaboration with NIST) has shown that more finely ground limestone (e.g., nano-limestone) has the potential to accelerate fly ash reactions thereby overcoming excessive retardation in high volume fly ash mixtures (8). This work showed that the time of setting could be regulated depending on the mean particle size of the limestone used. Recent work has examined the use of nano-limestone (9,10). Sun et al. (11) examined the use of jet-mill grinding as an alternative method to conventional grinding.

1.2 Research Objective

This project examines the potential impact of using cement with up to 15% of interground limestone (portland limestone cement) on the potential performance of concrete pavements and concrete in transportation structures. Since two state-of-the-art (SOTA) literature reviews have been conducted (one by the PI) in the last four years the work in this study will focus on the main areas that have been identified in those reports as requiring further study. In addition, this work will focus on providing a description of items that the Indiana Department of Transportation (INDOT) may need to consider in their specifications (especially in areas where ASTM C150 cements are currently specified) to better accommodate the potential use of these materials by INDOT. The following five items were the main areas investigated in this study.

1. Examining the influence of limestone size and method of cement replacement (interground or additive) on early age reactivity with and without fly ash.
2. Examining the influence of limestone on the mechanical properties of concrete.
3. Examining the influence of limestone on the transport properties of concrete.
4. Review the potential impact that these cements may have on INDOT practices and to discuss what/if any specifications should be modified to enable these cements to be used (provided positive data is obtained).
5. Developing educational modules for use at Road School that identifies the benefits of these materials as well as items that users may need to know.

It is the intention that this research will enable INDOT and INDOT contractors to better understand how to incorporate more sustainable materials in the construction of the transportation infrastructure. This will enable the increased use of 'greener' and potentially more cost effective materials to be used. The utilization

of the materials studied in this project has the potential to reduce the CO₂ per cubic yard of concrete and will extend the life of cement plant quarries.

1.3 Research Approach

This project utilized a fundamental approach to determine whether cement with up to 15% of interground or blended limestone can be used as an alternative to ordinary portland cement. The work was divided into seven main tasks, which have been laid out as separate chapters of this report. To complete the work, three commercially produced portland limestone cements were obtained that are currently interground. This is important since frequently the limestone is specifically ground at the mill to obtain a certain level of performance. It should be noted that in each case the parent clinker was compared to the same clinker where limestone was interground. An additional cement was tested where the limestone was blended (i.e., not interground) as needed, enabling better control of the size of the limestone. In addition, one of the commercially produced cements was used with fly ash. The following section describes each of the main tasks that the project covered in more detail.

Chapter 2: Literature Review

The first task of the project was to perform a literature review. Cements containing limestone have been in utilization for nearly three decades and are more recently becoming more popular in North America. The purpose of the literature review was to establish where and how these cements are being utilized and also to establish a frame of reference when evaluating the performance of the materials in the present study.

Chapter 3: Characterization of Materials in Systems Containing Limestone

Chapter 3 discusses the results from the characterization of the materials used in the study. An analysis of the cement compositions and particle size distributions is presented and the influence of the material characteristics on the overall performance of the concrete is discussed. This information highlights the inherent material differences between OPC, blended OPC with limestone, and interground PLC materials which help to explain the performance of concrete systems using these cements, leading to specific recommendations for specifying these cements.

Chapter 4: Evaluation of the Hydration Reaction

Chapter 4 examines the influence of portland limestone cements on the hydration reaction. Research is presented on the isothermal calorimetry (IC) and chemical shrinkage (CS) of these materials, showing the effects of limestone presence on the degree of hydration (DOH). X-ray diffraction (XRD) and

thermogravimetric analysis (TGA) combined with differential thermal analysis (DTA) were used to evaluate the reactivity of the limestone within the cement systems. This information shows the extent to which the limestone can be described as “inert”. In addition, this work extended the findings of each task to include systems that contain fly ash.

Chapter 5: Evaluation of the Mechanical Properties of Systems Containing Limestone Additions

Chapter 5 presents data on the mechanical properties of concretes containing limestone additions. The data presented in this chapter include the flexural and compressive strengths, the time of setting, and the static modulus of elasticity. These results can be used by INDOT to gauge the mechanical properties of concretes containing limestone made using local materials. In addition, a brief study on the volume change limestone cements is presented.

Chapter 6: Evaluation of the Transport Properties in Systems Containing Limestone Additions

The transport properties of systems with and without limestone were evaluated. Specifically the water absorption properties of these systems was assessed along with the electrical properties. The study was performed on a series of different water to cement ratios to determine which systems have similar performance in regards to durability. Finally, migration cell testing was conducted to compare the diffusion coefficients of systems containing limestone with those that do not.

Chapter 7: Summary, Conclusions, and Recommendations

Provide any recommendations on for INDOT to consider regarding the use of PLC.

2. LITERATURE REVIEW

2.1 Introduction

Recently, a few literature reviews have been performed to discuss the behavior and performance of portland cement containing limestone. These reviews include the performance of limestone cements containing various portions of limestone through either intergrinding or blending (2–4). This literature review seeks not to reproduce the same information that is already available; rather, it has been done to establish a frame of reference for the present research.

2.2 Current Specification of Limestone Replacements in Cement

2.2.1 Europe

Portland limestone cement (PLC) has been utilized for multiple decades in Europe by countries such as

Spain, France, and Germany, but it was not universally standardized until the year 2000. EN 192-1 (12) defines three different classes of cements containing limestone. CEM I may contain up to 5% limestone (defined as a minor additional constituent), CEM II/A-L and CEM II/A-LL contain between 6% and 20% limestone (by mass), while CEM II/B-L and CEM II/B-LL contain between 21% and 35% limestone. It is important to note that the European standard divides cements into different strength classes, acknowledging the potential performance implications that dilution has on reducing strength when limestone is added to ordinary portland cement. Type CEM I cements are considered ordinary portland limestone cements while type CEM II cements are termed to be portland composite cements. Limestone can also be included within the composite cement classes of CEM II/A-M and CEM II/B-M. The ‘-M’ designation denotes that multiple ingredients may be present, where in many cases ground limestone is added along with a supplementary cementitious material such as blast furnace slag or fly ash.

The limestone utilized in any of these cements must meet specified criterion. The calcium carbonate (CaCO_3) content calculated from the calcium oxide (CaO) content shall be greater than 75% by mass. To control the clay content of the limestone, the methylene blue index (MBI) shall not exceed 1.2% (1.2 g/100 g). Lastly, the total organic carbon (TOC) content may not exceed 0.20% by mass (designated by -LL) or 0.50% by mass (designated by -L).

2.2.2 Canada

The Canadian cementitious materials compendium originally introduced the utilization of portland limestone cements in 2008 and later amended these provisions in 2010. CSA A3000 (13) defines four classes of cements containing limestone. Cement Type Gu, a general use ordinary portland cement may contain up to 5% (by mass) of minor additions, which may take the form of limestone. Similarly, Type GuB is an ordinary portland cement blended with other supplementary materials which may also contain up to 5% of limestone. Type GuL and GuLb cements, a general use portland limestone cement and blended portland limestone cement, respectively, may contain between 5% and 15% (by mass) of limestone. The standard prohibits any further percentages of ground limestone beyond 15% in efforts to ensure comparable performance to ordinary portland cements, as Type Gu and GuL must meet the same prescribed physical requirements, shown in Tables 4 and 6 of CSA A3001-08. These physical requirements include maximum fineness, initial set times, and compressive strengths.

CSA places chemical requirements on cements. The maximum loss on ignition for Type GuL is set at 10% in contrast with a maximum of 3% for type Gu cements. This difference acknowledges the liberation of large percentages of CO_2 from the limestone during ignition. The limestone utilized for the production of

portland limestone cements must also meet similar criterion as that of EN 192-1. The CaCO_3 must be greater than 75% as calculated by CaO content and mbi must be less than 1.2%. CSA has only one class of permitted TOC's, setting the limit for all limestone used at 0.5% by mass.

2.2.3 United States of America

In the United States, ASTM C150 (14) permits the inclusion of up to 5% (by mass) of finely ground limestone. The limestone must be naturally occurring and consist of at least 70% (by mass) of one or more of the mineral forms of calcium carbonate. Portland limestone cement has been used in North America under the ASTM C1157 (15) specification, but during the course of this project, the inclusion of up to 15% (by mass) of finely ground limestone was provisionally passed under the harmonized ASTM/AASHTO standard (ASTM C595-12 (16), AASHTO M240-12 equivalent).

2.3 Mechanisms Associated with Limestone Replacements in Cement

The replacement of cement by ground limestone directly impacts the overall cement composition and hydration. The effects of limestone have been observed to alter aspects of the cement performance through the proposed mechanisms of dilution, the filler effect (particle packing), and nucleation (4,6,17–23). Many authors have observed that these mechanisms affect the hydration of the cement, subsequently modifying the performance of the overall system (4,6,17–26). It is important to note that these mechanisms are inter-related and act simultaneously, influencing many of the same parameters of the system. In general, it can be considered that the filler effect and nucleation work in tandem while opposing the effects dilution. A description of each of the mechanisms and their potential implications toward the behavior of the hydration and performance of cementitious systems is discussed in the following sections.

2.3.1 Dilution

When cement is replaced by limestone, a natural dilution of cement clinker is observed. For a given water-to-powder ratio (w/p), increasing percentages of limestone replacement result in greater dilution of the cement. This dilution results in a higher effective water-to-cement ratio (w/c) in a unit volume, which can lead to increased cement hydration at earlier ages (27) as well as increased initial porosity. The increased hydration can provide higher strengths to counter the reduction in reactant products. At later ages, the reduction in cement content due to dilution can lead to lower cumulative heat of hydration.

The initial porosity can be determined using Powers' gel space theory (28). Irassar has shown that

a threshold for maximum/optimum limestone replacement percentage exists at any w/c, above which additional porosity is introduced from any further addition of water (24). The added capillary porosity is created by the addition water beyond what is necessary for the cement grains to fully hydrate. This excess water occupies space between the hydration products, which will form empty porosity. At cement replacements of up to 15%, the addition of limestone directly affects the overall pore structure development, which controls the rate of (and subsequently ultimate) strength development. Furthermore, the pore structure dictates the rate at which exterior species (particularly water, salts, and sulfates) can ingress into the system, leading to potential deterioration through mechanisms such as freezing and thawing, scaling, and sulfate attack.

2.3.2 Filler Effect

If it is assumed that the finely ground limestone acts as an inert filler when combined with clinker, there can still be benefits associated with limestone as it acts as a filler. The effects of the inclusion of limestone impact the hydration and performance of the cement in two important ways. The first is that the particle size distribution (PSD) is altered, and subsequently the interparticle spacing changes and surface area of the particles changes. The net effect of the altered PSD depends strongly on the method in which the limestone was added to the cement. In commercial practices, the limestone will be interground with the cement clinker during the grinding process at the mill. Some have argued that resulting cement is one which has a wider PSD, with the majority of the limestone occupying the smallest sizes within the composite cement (29).

This is due to the limestone being a softer material than the clinker. When the two materials are ground together in the ball mill, the limestone is pulverized more easily, resulting in generally smaller particle sizes than the clinker. The filler effect implies that the small particles may inhabit the smallest pore spaces, thereby filling in pores where the clinker would not. The overall effect is an improved PSD that encompasses a wider distribution and does not have gaps across this distribution (29–31). The alternative method for including limestone in cement is by replacing a portion of the cement with a separately ground limestone. The result is referred to as a blended cement, as a finely ground limestone would be blended with the cement at the time of mixing. In contrast to intergrinding, blending limestone with cement does not produce a wider and smoother particle distribution. Typically, the limestone will be ground to an average particle size, and when added to cement, it will only inhabit spaces corresponding to the sizes to which it was ground (11). Thus, the net effect of blended limestone cements is a function of the particle size of the ground limestone and the PSD of the base cement. It is important to note that much of

the early research done was on blended limestone cements.

Particle size distribution affects both the interparticle spacing and the surface area of the particles. When the PSD is wider and smoother, the cement will exhibit improved particle packing. The result is a more efficient use of space, eliminating the initial porosity that must be filled with hydration products during hydration. The decrease in porosity tends to lead to a higher strength and improved transport properties, but as Bentz and Peltz (17) note, the tighter particle spacing leaves smaller pores, which as they empty from further hydration, can increase the shrinkage of the material at early ages. Based on this idea, it has been suggested that one potential way to reduce shrinkage is to include coarsely ground limestone to take advantage of larger interparticle spacing as well as reduced heats of hydration (5). The influence of PSD on the surface area of the particles has a wide range of influences on the performance of the system. Greater surface area will lead to increased rates of reaction as well as increase the demand for water while also affecting the workability of the material.

2.3.3 Nucleation

The limestone particles within the cement act as nucleation sites during cement hydration. Nucleation occurs due to the lower surface energy of the smaller particles of limestone included within the clinker. These particles act as a preferential place for the precipitation of calcium hydroxide (CH), which in turn promotes the hydration of the clinker phases at early ages. It is also important to realize that since the CH is preferentially forming on the surfaces of the limestone particles, there is a potential for the formation of large CH crystals (32), which can have potentially negative impacts on the performance of the concrete. Overall, the result of nucleation is an increased rate and degree of hydration at early ages.

2.3.4 Net Effects of Combined Mechanisms

Together, dilution, the filler effect, and nucleation can alter the behavior of the cementitious system. As it was discussed, the dilution effect, a function of the percentage of cement replaced by limestone, can alter the initial porosity reducing strength. The filler effect, a function of particle size distribution, can reduce the initial porosity of the system while increasing the early rates of hydration and strength. Nucleation, a function of surface energy, also increases the rates of early hydration. Together, the net effects of these three mechanisms will alter the initial porosity of the system and increase the rate of initial rate of hydration while reducing the cumulative heat of hydration. These characteristics are crucial in the development of early age properties, and it is clear that if similar performance of PLC's is desired, these mechanisms must be properly controlled.

2.4 Summary and Conclusions

As the literature has shown, the replacement of cement by up to 15% of ground limestone can have large implications on the performance of a cementitious system. Through the careful control of the mechanisms of dilution, filler effect, and nucleation, it is clear that the performance of PLCs can be tuned to meet specific needs. By controlling the particle size distribution and fixing the maximum limestone replacement content to 10%–15%, the properties of PLCs can demonstrate comparable performance to their OPC counterparts.

3. CHARACTERIZATION OF MATERIALS IN SYSTEMS CONTAINING LIMESTONE

3.1 Introduction

The goal of replacing a portion of cement with ground limestone is to reduce clinker contents in concrete production. Before assessing the performance of these materials, it is necessary to understand the constituent materials. The purpose of this chapter is to characterize the cements and supplementary materials used in this study. Furthermore, the method of limestone inclusion (i.e., intergrinding or blending) is investigated and the resulting effects on initial particle packing of the system are discussed.

3.2 Materials and Methods

3.2.1 Materials

Three commercially produced portland limestone cements (PLCs) were used in this study and compared to ordinary portland cements (OPCs) produced at respective mills and were manufactured from the same clinker. An additional cement was blended with a finely ground limestone powder to control the size of limestone in the cementitious system. This was done for two different mean particle sizes of limestone: one being coarser with a mean particle size of 10.8 μm (designated coarse limestone (CL)) and one being finer with a mean particle size of 1.3 μm (designated fine limestone (FL)). Finally, one of the commercial interground PLCs was used with a fly ash (FA) to create a ternary blended system. The naming conventions for the cementitious systems can be seen in Table 3.1.

3.2.2 X-ray Diffraction

X-ray diffraction (XRD) combined with Rietveld fitting was used to determine the phases present in each cementitious system and the content of each phase in the unhydrated state. The testing was conducted with a Bruker D8 instrument with a $\text{CuK}\alpha$ source ($\lambda = 1.54 \text{ \AA}$) at 40 kV and 40 mA, with the Rietveld fitting being performed using Maud software (11,33,34). The XRD testing was performed directly on the dry powders.

3.2.3 Thermogravimetric Analysis and Differential Thermal Analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to determine the quantity of calcite (CaCO_3) of each cementitious system. In the present work, TGA/DTA analyses were performed on the dry powders using a SDT-2960 simultaneous DTA-TGA device. The equipment simultaneously recorded the sample weight change and associated heat transfer with the sample. The content of CaCO_3 was determined from the mass loss between 600–780 $^\circ\text{C}$ (35). The testing was performed on powders of about 50 mg, with alumina powder used as a reference. The materials were heated from 30 to 1100 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$. During the test, the chamber was purged with N_2 at 110 ml/min.

3.2.4 Scanning Electron Microscopy

Back-scattered electron (BSE) imaging and element mapping techniques were used in scanning electron microscopy (SEM) to determine the shapes, sizes, and elements of the cementitious systems. The samples were prepared by blending approximately 10 g of powder with an epoxy resin to form a viscous paste, which was transferred into a 10 mm diameter x 55 mm tall glass container and cured at 23 $^\circ\text{C}$ for one day. The cured specimen was then cut with a low-speed saw to obtain a plane surface and then subsequently polished using 15, 9, 3, 1, and 0.25 μm diamond paste for 4 min each on top of a polishing cloth. Before loading the samples into the SEM chamber, the samples were gold coated to form a conductive surface. The SEM was performed on a FEI Quanta 3D with field emission gun working at 12 kV. The collection time for element mapping was 2 hrs.

3.2.5 Particle Size Distribution and Blaine Fineness

The particle size distribution (PSD) of each material was measured by a Coulter LS32 laser sizer with high reproducibility (<1%). Ethanol was used as a dispenser. The density required for PSD calculations was determined using a MicroMeritics AccuPyc 1330 Pycnometer.

TABLE 3.1
Material naming convention and description

Material	Description
OPC 1	Commercially produced ordinary portland cement (OPC)
OPC 2	
OPC 3	
PLC 1	Commercially produced portland limestone cement (PLC)
PLC 2	
LC 3	
OPC 4	OPC blended with ground limestone
CL	Coarsely ground limestone powder
FL	Finely ground limestone powder
FA	Fly ash

The Blaine fineness was also determined in order to compare the associated increase in surface area of interground PLCs. A Blaine permeability apparatus was used to perform this test following ASTM C204-11 (36).

3.3 Results and Discussions

3.3.1 XRD

The XRD spectra of the materials are shown in Figure 3.1, with the phases indicated on Figure 3.1b for OPC 2 and PLC 2. Similar phases were observed in the other OPC/PLC powders and were not indicated here. In Figure 3.1 (a), (b), and (c), the XRD pattern of the PLCs show peaks that appear to be from either the raw limestone or the corresponding OPC (i.e., no new peaks are found), therefore suggesting that the intergrinding is primarily a physical process that does not appear to result in any chemical alterations.

The mineral compositions of the OPC materials were obtained from Rietveld fitting of the XRD spectrum and are listed in Table 3.2. In the OPCs, very little CaCO_3 was observed within the resolution of XRD spectra, which was likely due to the preferential orientation of crystal planes of the Rietveld fitting method. The values have been presented in Table 3.2 for reference; however a more reliable CaCO_3 content was determined by the TGA/DTA method and is presented in the following section.

3.3.2 DTA/TGA to Determine the Content of Limestone

The content of CaCO_3 in the OPC and PLC materials was calculated from the TGA/DTA results shown in Figure 3.2, Figure 3.3, Figure 3.4, Figure 3.5, and Figure 3.6, and is listed in Table 3.3. The weight loss between 600 and 780 °C (550~950 °C for CL and FL, determined by the DTA curves) was associated with a decomposition of CaCO_3 , and was therefore used to determine the calcite contents of each material. The results show that the CaCO_3 levels for each OPC ranged from approximately 0.5% to just under 3% (by mass). The interground PLCs were determined to have CaCO_3 levels ranging from 7.5% to 10.5%, however it should be noted that the limestone used in the productions of these PLCs are permitted to have CaCO_3 contents as low as 75%. These impurities in the limestone suggest that the actual limestone filler content in the PLCs may have ranged between approximately 10% and 14%. The CL and FL contain no less than 97% CaCO_3 indicating that the CL and FL are nearly pure calcite.

3.3.3 Particle Size Distribution and Blaine fineness

The cumulative particle size distributions for each material are shown in Figures 3.7, 3.8, 3.9, 3.10, and 3.11 with the differential PSDs shown in Figure 3.12. The mean particle sizes and densities are shown in Table 3.4. The replacement of cement with limestone

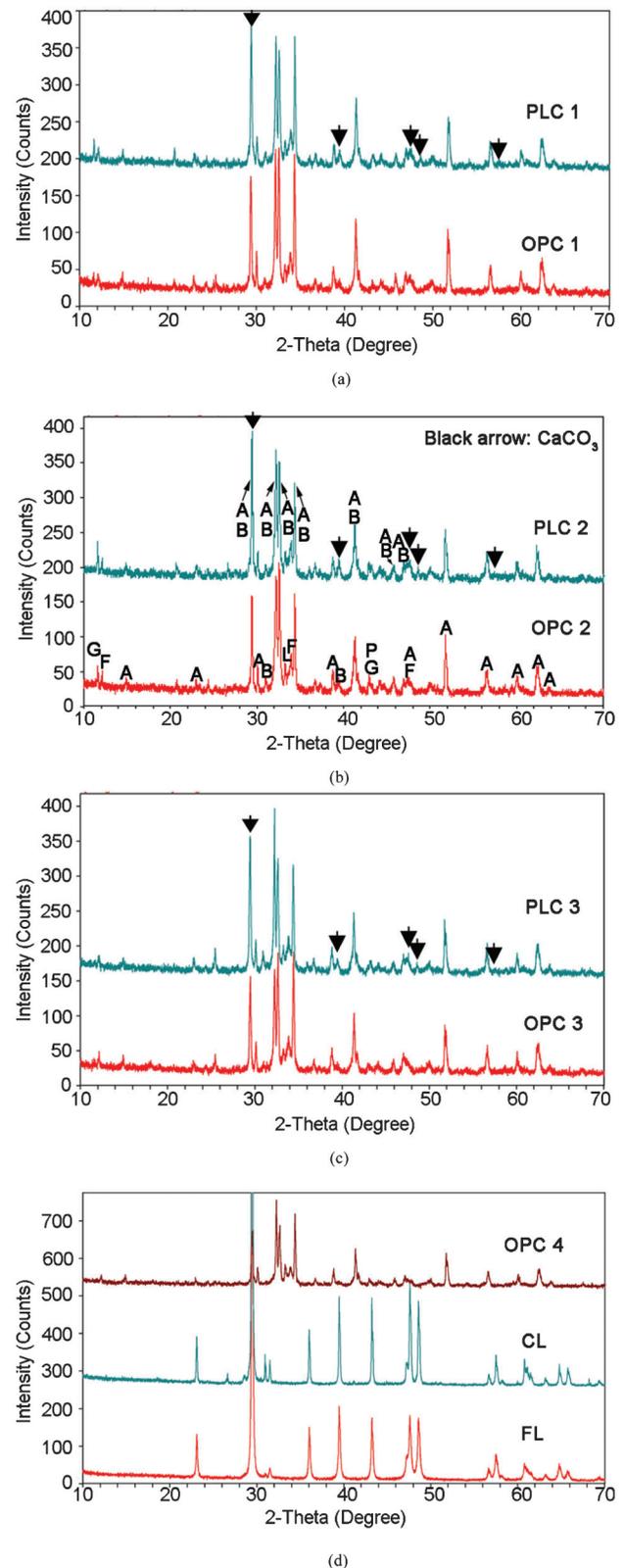


Figure 3.1 XRD spectra of (a) OPC 1 and PLC 1, (b) OPC 2 and PLC 2, (c) OPC 3 and PLC 3, and (d) OPC 4, CL, and FL. Phases are labeled A= C_3S (alite), B= C_2S (belite), L= C_3A (aluminates), F= C_4AF (ferrite), G=gyypsum, P=MgO (periclase); black arrow indicates CaCO_3 (calcite) phase.

TABLE 3.2
Compositions of the OPC materials

Cement	C ₃ S (%)	C ₂ S (%)	C ₃ A (%)	C ₄ AF (%)	MgO (%)	Gypsum (%)	CaCO ₃ (%)
OPC 1	54.08	27.14	2.13	11.6	0.52	2.81	0.00
OPC 2	42.42	34.08	3.28	12.38	2.28	2.48	1.73
OPC 3	59.21	15.07	2.66	16.43	1.79	2.63	0.00
OPC 4	65.95	9.37	6.07	14.71	2.18	1.25	0.00

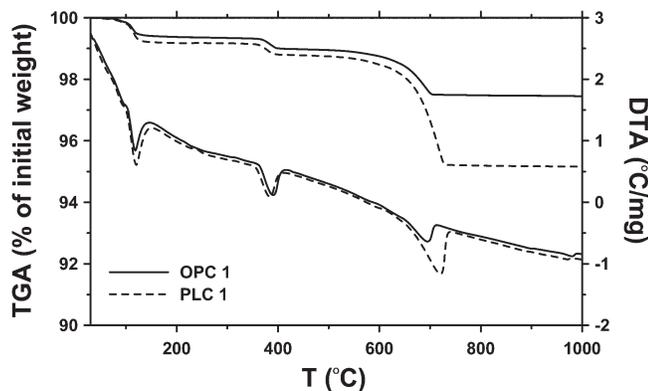


Figure 3.2 DTA/TGA data of OPC 1 and PLC 1.

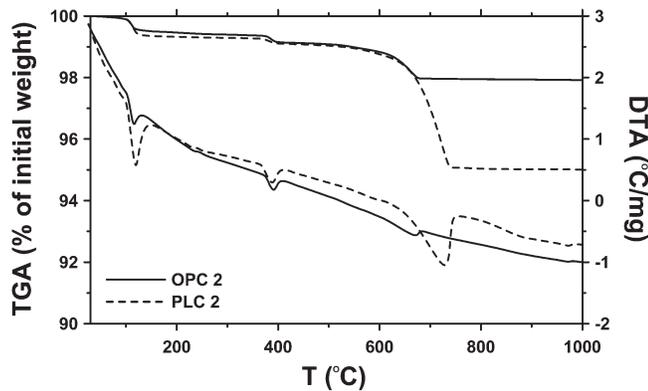


Figure 3.3 DTA/TGA results for OPC 2 and PLC 2.

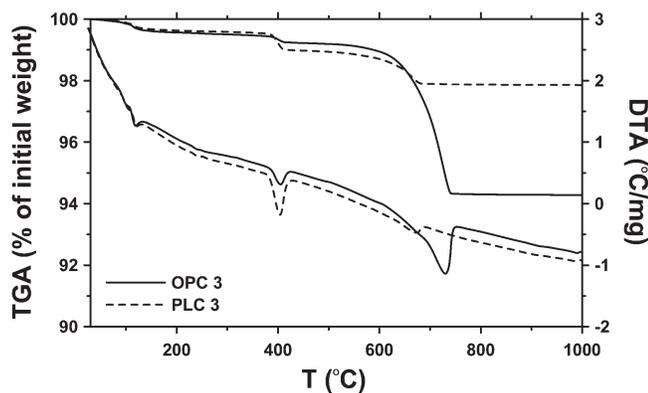


Figure 3.4 DTA/TGA results for OPC 3 and PLC 3.

TABLE 3.3
Content of CaCO₃ in each material

Material	CaCO ₃ (wt %)
OPC 1	2.88
PLC 1	7.45
OPC 2	2.02
PLC 2	8.42
OPC 3	1.89
PLC 3	10.55
OPC 4	0.49
CL	97.15
FL	99.49

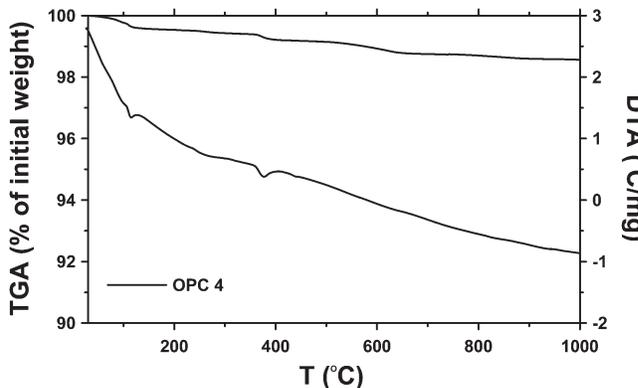


Figure 3.5 DTA/TGA results for OPC 4.

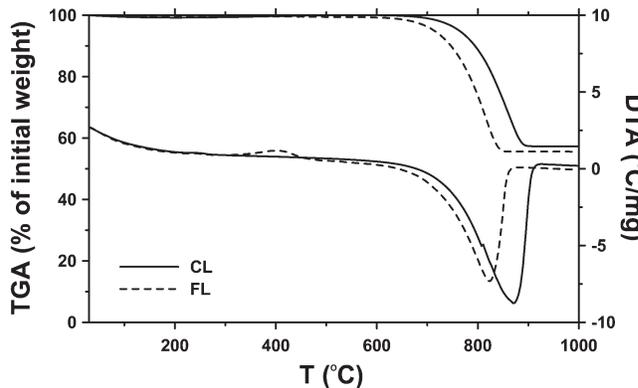


Figure 3.6 DTA/TGA results for CL and FL.

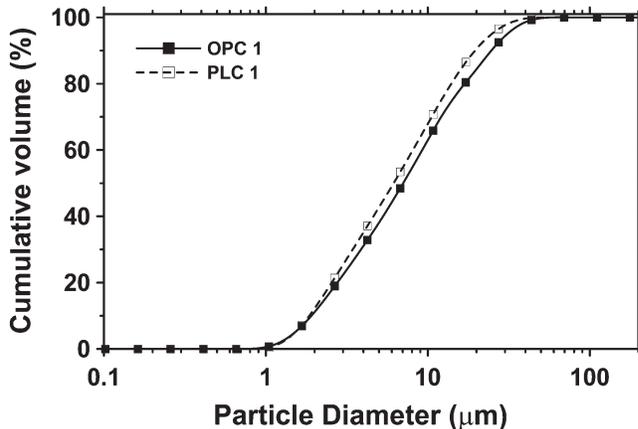


Figure 3.7 PSD of OPC 1 and PLC 1.

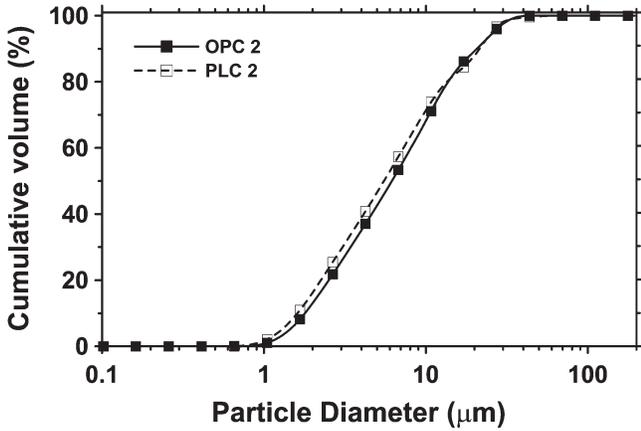


Figure 3.8 PSD of OPC 2 and PLC 2.

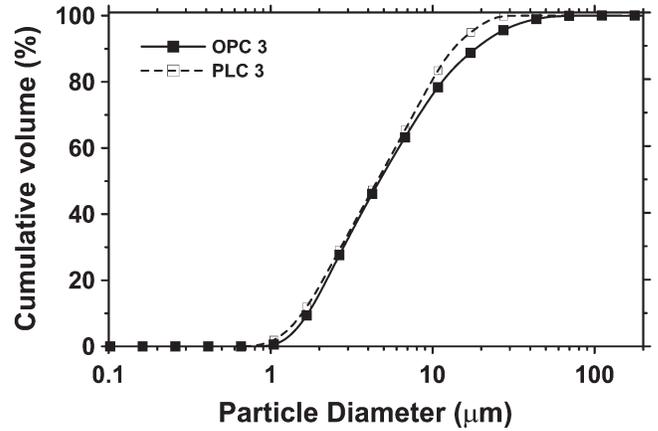
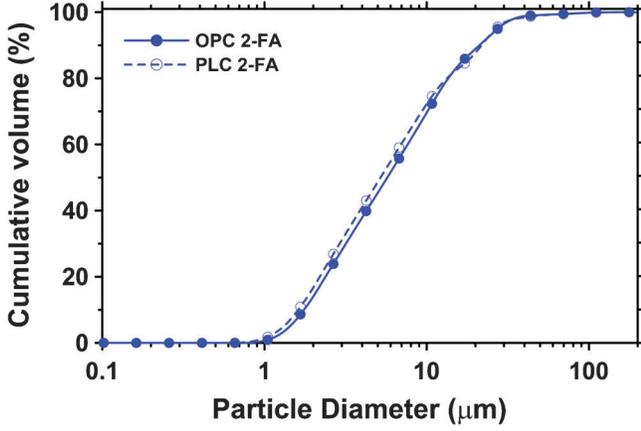


Figure 3.10 PSD of OPC 3 and PLC 3.

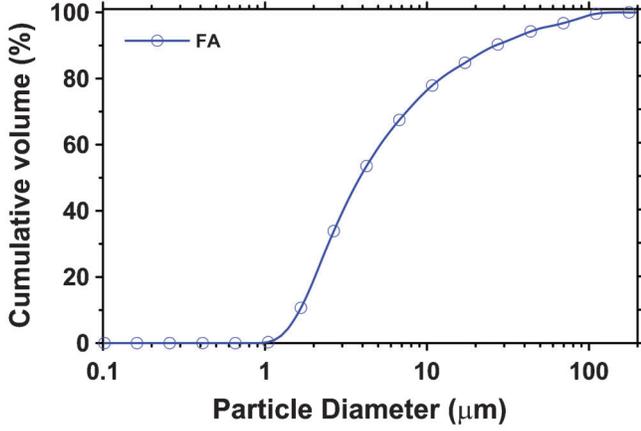
through intergrinding shifts the particle sizes such that there are in general fewer large cement particles and more fine particles, as seen in Figure 3.12. This shift exposes more surface area available for the hydration reactions, and results in closer interparticle spacing across all particle sizes.

In contrast to this, when the limestone is blended with the cement (i.e., not interground), the resulting

particle size distribution does not undergo the shift (reducing large cement particles and adding fine limestone powders) as is typically the case with the PLCs. Instead, these systems have the same volume percentage of very large cement grains but now also contain additional unreactive limestone particles aggregated

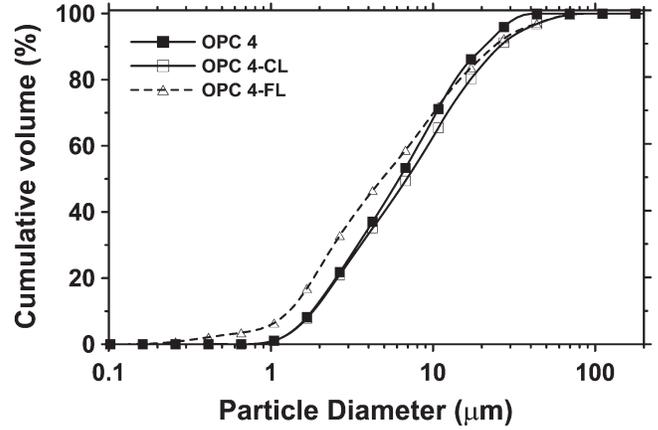


(a)

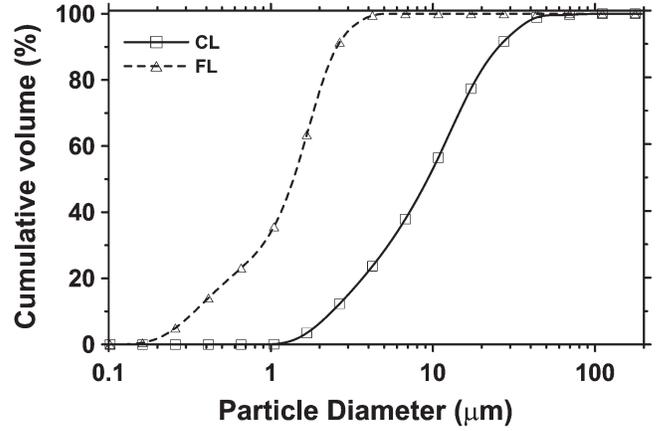


(b)

Figure 3.9 PSD of (a) OPC 2-FA and PLC-FA and (b) FA.



(a)



(b)

Figure 3.11 PSD of (a) OPC 4, OPC 4-CL, and OPC 4-FL and (b) CL and FL.

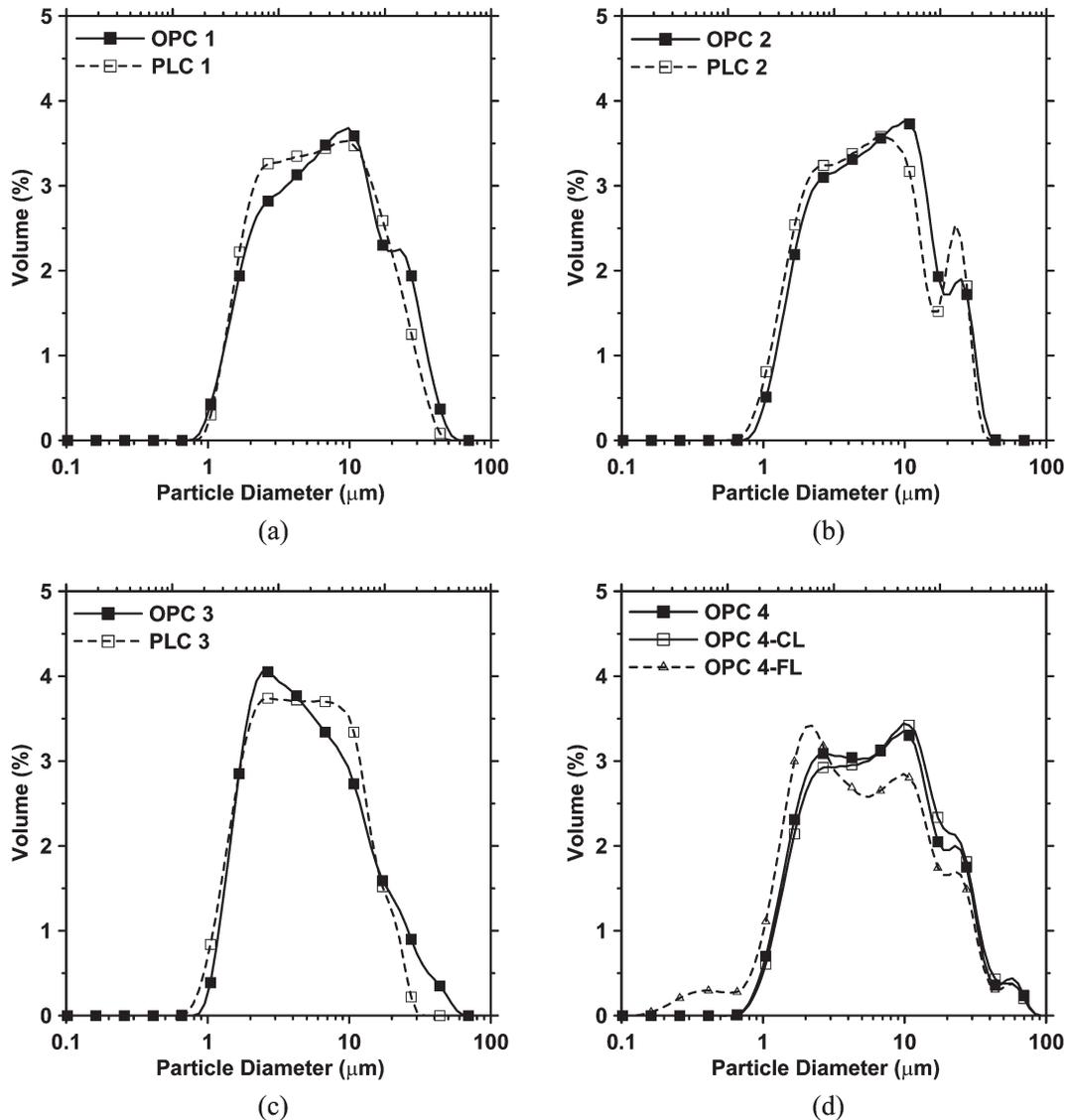


Figure 3.12 Differential pore size distribution determined by laser diffraction for (a) OPC 1 and PLC 1, (b) OPC 2 and PLC 2, (c) OPC 3 and PLC 3, and (d) OPC 4, OPC 4-CL, and OPC 4-FL.

around a small range of particle sizes. This suggests that the initial interparticle spacing may increase or decrease depending on the size of limestone particles. It is this

TABLE 3.4
Mean particle size and density of each material

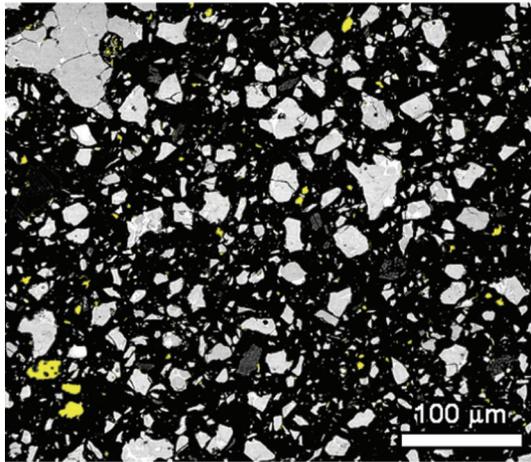
Material	Mean size (μm)	Density (g/cm^3)
OPC 1	9.40	3.12
PLC 1	7.89	3.12
OPC 2	7.93	3.16
PLC 2	7.68	3.11
OPC 3	7.14	3.17
PLC 3	5.65	3.13
OPC 4	9.85	3.17
CL	10.84	2.70
FL	1.30	2.70
FA	9.75	2.74

key distinction that will help to explain the difference in behavior of the interground and blended systems as they hydrate. It should be noted here that the ground limestone particles used had a mean particle sizes of 10.84 μm for the CL and 1.3 μm for the FL.

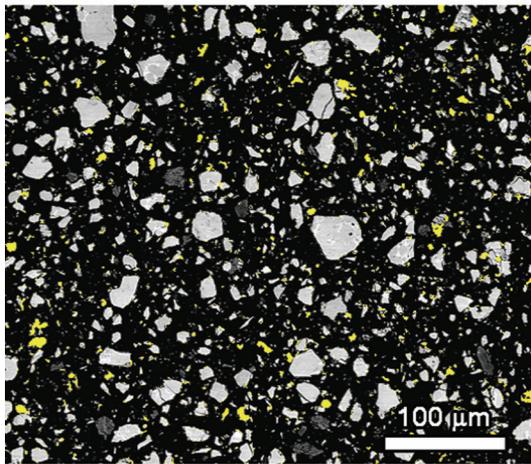
The Blaine fineness of each material is listed in Table 3.5. As was previously mentioned, the replacement of cement with ground limestone causes the need for the materials to be ground finer to have similar performance. For this study, the increase in surface area for PLCs 1 and 2 was approximately 15%, while PLC 3 was ground 32% finer.

3.3.4 Scanning Electron Microscopy

The BSE images of each limestone system and its corresponding OPC as well as the FA, CL, and FL are



(a)



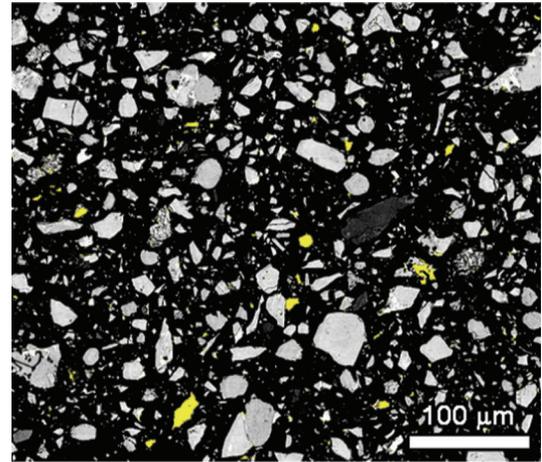
(b)

Figure 3.13 BSE image of (a) OPC 1 and (b) PLC 1.

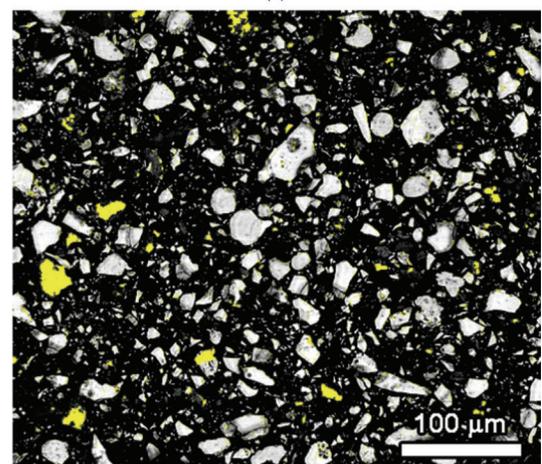
shown in Figures 3.13, 3.14, 3.15, 3.16, and 3.17. The CaCO_3 was identified by using elemental mapping in conjunction with gray levels, which was done to avoid confusion between the similar grey levels of gypsum and limestone during the analysis. Using the sulfate to distinguish the gypsum from the CaCO_3 , the calcite present in each cementitious system was identified and

TABLE 3.5
Blaine fineness of materials

Material	Blaine fineness (m^2/kg)	Increase of Surface Area (PLC/Control) (%)
OPC 1	384	—
PLC 1	452	18%
OPC 2	376	—
PLC 2	430	14%
OPC 3	392	—
PLC 3	518	32%
OPC 4	377	—
CL	321	—
FL	1069	—
FA	331	—



(a)



(b)

Figure 3.14 BSE image of (a) OPC 2 and (b) PLC 2.

is indicated as yellow on the images. In general, a smaller particle size can be observed in the interground PLCs in comparison to corresponding OPCs. Furthermore, it can be noticed that the CaCO_3 particles are generally smaller than the calcium silicate particles and the majority of the limestone occupies the smallest particle size regions. This is due to the softer nature of the CaCO_3 and is consistent with previous findings (37). The particle size of CL is larger than that of OPC 4 and FL is smaller than that of OPC 4, consistent with the PSD results. Detailed BSE and element mapping results can be found in the appendix.

3.4 Summary and Conclusions

This chapter discussed the characterization of cementitious systems containing limestone. The observations made here can be summarized as:

- XRD characterization showed that the intergrinding of PLC is primarily a physical process that does not appear to result in any chemical alterations.
- DTA/TGA showed that the commercially available PLCs contained approximately 10 to 14% of limestone.

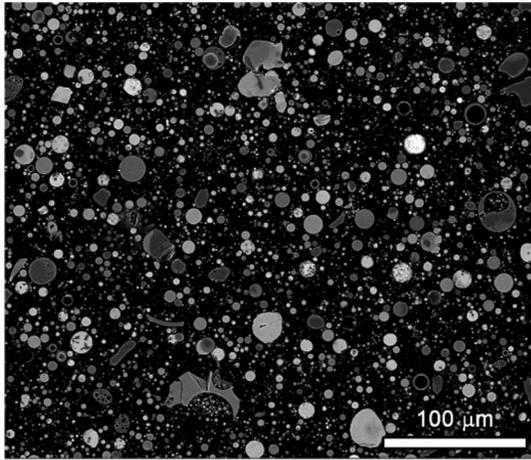
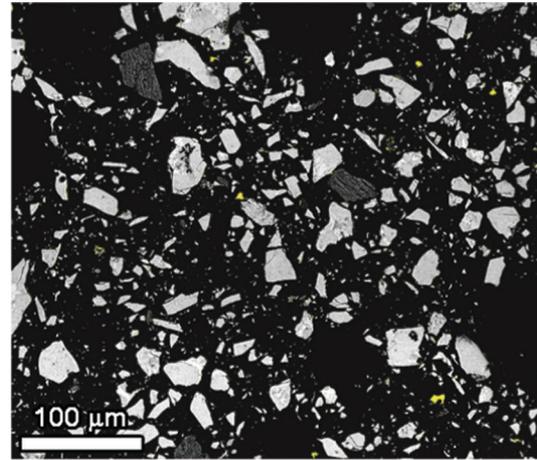
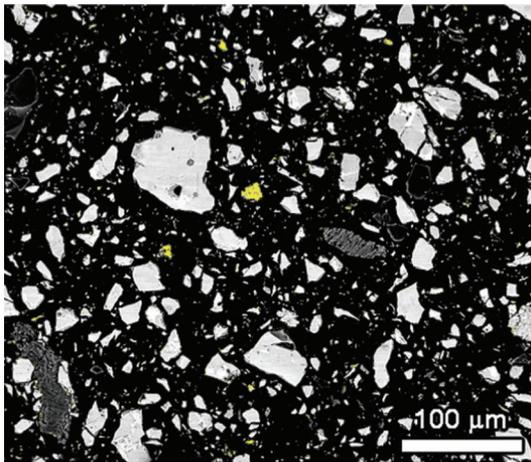


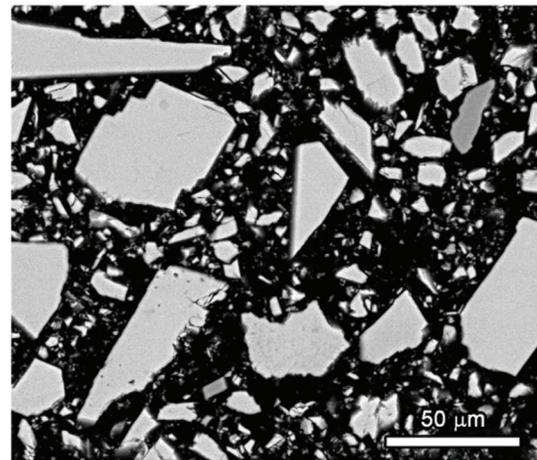
Figure 3.15 BSE image of FA.



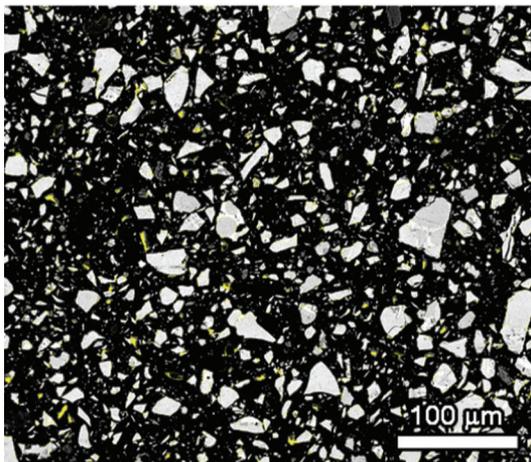
(a)



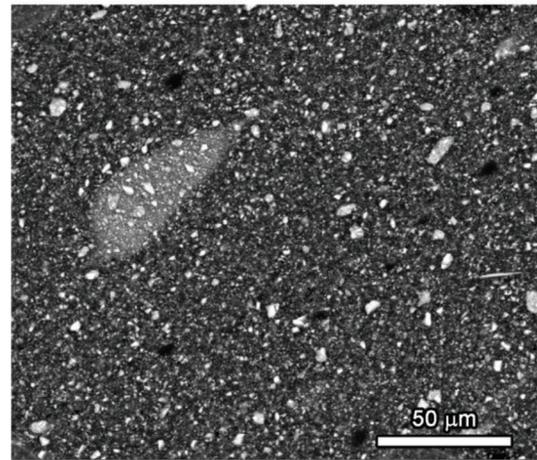
(a)



(b)



(b)



(c)

Figure 3.17 BSE image of (a) OPC 4, (b) CL, and (c) FL.

Figure 3.16 BSE image of (a) OPC 3 and (b) PLC 3.

- Intergrinding the limestone with the clinker results in a reduction in the coarser particles ($>20\mu\text{m}$). When the limestone is blended with cement, the resulting particle size distribution has an increase in particles of a specific size range (depending on the mean particle size of limestone used) with no reduction in coarser particles.
- The specific surface area (Blaine fineness) of PLCs increased by more than 14% in comparison to corresponding OPCs.
- SEM images showed that the limestone is ground finer than the cement grains, with the majority occupying the smallest size regions.

4. EVALUATION OF THE HYDRATION REACTION

4.1 Introduction

The goal of using portland limestone cements (PLCs) is to provide a suitable replacement for Type I and Type I/II ordinary portland cements (OPCs) that achieve similar performance. While the performance of these materials will be addressed in subsequent chapters, this chapter presents results on the study of the hydration reaction of cements containing limestone. In addition, the hydration of these systems in the presence of fly ash was also studied. The mechanisms of dilution, the filler effect, and nucleation are discussed using the results of various testing techniques to determine the significance of each on the hydration of these cementitious systems. The results herein highlight the change in hydration kinetics that PLCs exhibit which are in turn used to explain how similar performance may be achieved.

4.2 Materials and Methods

4.2.1 Materials

Three commercially produced, ASTM C150 Type I/II (I) ordinary portland cements (OPC 1-3) with complimentary ASTM C595 Type IL (I6) portland limestone cements (PLC 1-3) containing 10% to 15% replacement of cement by limestone through inter-grinding were studied. An additional commercially produced ASTM C150 Type I/II cement (OPC 4) was used with ground limestone powders of varying fineness to create blended limestone cements (OPC 4-CL and OPC 4-FL). The cement compositions can be seen in Table 3.2. The mean particle sizes, density, Blaine fineness, and percentage of calcium carbonate (CaCO_3) content by weight (if any) are summarized in Table 4.1. The two ground limestone powders used had mean particle sizes of 1.3 μm (fine limestone, FL) and 10.8 μm (coarse limestone, CL). The fine aggregate used was a normal weight natural river sand with a specific gravity of 2.58 and an absorption of 1.7% by mass. Tempered

TABLE 4.1
Mean particle size, density, Blaine fineness, and calcite content for each material

Material	Mean size (μm)	Density (g/cm^3)	Blaine fineness (m^2/kg)	CaCO_3 (wt %)
OPC 1	9.4	3.12	384	2.9
PLC 1	7.9	3.12	452	7.5
OPC 2	7.9	3.16	376	2.0
PLC 2	7.7	3.11	430	8.4
OPC 3	7.1	3.17	392	1.9
PLC 3	5.7	3.13	518	10.6
OPC 4	9.9	3.17	377	0.5
CL	10.8	2.70	321	97.2
FL	1.3	2.70	1069	99.5
FA	9.8	2.74	331	—

tap water at 23 ± 2 °C was used as the mixing water and a high range water reducing agent (HRWRA) was added at varying rates in order to achieve roughly equivalent consistency between mixtures. It should be noted that these rates were not based on any rheological testing of the mixtures.

4.2.2 Mixture Proportions

The mortar mixtures used in the study of the hydration reaction are shown in Table 4.2. The design of these mixtures is based on the concrete mixture designs implemented in chapters 5 and 6 of this report, using equivalent proportions while omitting the coarse aggregate. This study assessed eleven different cement systems at three water-to-powder ratios (w/p) for a total of thirty-three different mixtures. As mentioned, a total of four ordinary portland cements (OPCs), three complimentary portland limestone cements (PLCs), and two blended limestone cements were used to assess the effects of ground limestone additions in cementitious systems. Both of the blended limestone cements (OPC 4-FL and OPC 4-CL) had 15% of the cement replaced (by volume) with ground limestone. In order to assess the effects of fly ash on PLC's, two additional cement systems were created by replacing 20% of the cement (by volume) in either OPC 2 or PLC 2 with a class C fly ash (FA). All eleven of these cement systems were evaluated at water-to-powder ratios (w/p) of 0.38, 0.42, and 0.46, corresponding to water-to-cement ratios (w/c) of approximately 0.41, 0.45, and 0.49 for PLC's and blended limestone cements. Each mortar mixture had a fine aggregate volume fraction of approximately 58%. The naming convention for each mixture follows the format of [w/p – (OPC/PLC) # – (FA/CL/FL)], where FA signifies a fly ash replacement, CL denotes a blended limestone-cement system with coarsely ground limestone, and FL denotes a blended limestone-cement system with finely ground limestone.

In certain test applications, mortar specimens were not suitable due to the relative size of the aggregate. In these cases, equivalent paste fractions were made using the same mixture designs as previously described, however the coarse aggregate was omitted and the batching water was adjusted to only account for the water necessary for cement hydration.

4.2.3 Mixing Procedure

All specimens utilized in this chapter were prepared in a Renfert Twister EvolutionTM 120v vacuum mixer. The fine aggregate (if any) was prepared in the oven dry state and first combined with the binder for approximately 15 s. The mixing water (including water for the absorption of the aggregates) was then added and the materials were mixed for 30 s at a speed of 350 rpm. The mixing bowl was then removed, scraped with a spoon, and any HRWRA was added. The materials were then mixed for an additional 2 min at 400 rpm.

TABLE 4.2
Mixture proportions and naming conventions

Mixture	Water/ Powder (w/p)	Water/ Cement (w/c)	Ordinary Portland Cement (lbs/yd ³)	Portland Limestone Cement (lbs/yd ³)	Ground Limestone (by Volume) (%)	Fly Ash (by Volume) (%)	HRWRA (fl oz/cwt)
0.38-OPC 1	0.38	0.38	604	—	—	—	11.4
0.42-OPC 1	0.42	0.42	571	—	—	—	5.7
0.46-OPC 1	0.46	0.46	542	—	—	—	1.4
0.38-PLC 1	0.38	0.41	—	598	—	—	11.4
0.42-PLC 1	0.42	0.45	—	566	—	—	5.7
0.46-PLC 1	0.46	0.49	—	537	—	—	2.8
0.38-OPC 2	0.38	0.39	604	—	—	—	11.4
0.42-OPC 2	0.42	0.43	571	—	—	—	5.7
0.46-OPC 2	0.46	0.47	542	—	—	—	1.4
0.38-OPC 2-FA	0.38	0.47	494	—	—	20	7.1
0.42-OPC 2-FA	0.42	0.52	467	—	—	20	2.8
0.46-OPC 2-FA	0.46	0.57	443	—	—	20	0.7
0.38-PLC 2	0.38	0.41	—	598	—	—	11.4
0.42-PLC 2	0.42	0.46	—	566	—	—	5.7
0.46-PLC 2	0.46	0.50	—	537	—	—	1.4
0.38-PLC 2-FA	0.38	0.50	—	486	—	20	8.5
0.42-PLC 2-FA	0.42	0.56	—	460	—	20	5.7
0.46-PLC 2-FA	0.46	0.61	—	437	—	20	2.8
0.38-OPC 3	0.38	0.38	604	—	—	—	11.4
0.42-OPC 3	0.42	0.42	571	—	—	—	5.7
0.46-OPC 3	0.46	0.46	542	—	—	—	1.4
0.38-PLC 3	0.38	0.41	—	598	—	—	11.4
0.42-PLC 3	0.42	0.45	—	566	—	—	5.7
0.46-PLC 3	0.46	0.49	—	537	—	—	1.4
0.38-OPC 4	0.38	0.38	604	—	—	—	11.4
0.42-OPC 4	0.42	0.42	571	—	—	—	5.7
0.46-OPC 4	0.46	0.46	542	—	—	—	1.4
0.38-OPC 4-CL	0.38	0.44	521	—	15	—	11.4
0.42-OPC 4-CL	0.42	0.48	493	—	15	—	5.7
0.46-OPC 4-CL	0.46	0.53	468	—	15	—	2.8
0.38-OPC 4-FL	0.38	0.44	521	—	15	—	11.4
0.42-OPC 4-FL	0.42	0.48	493	—	15	—	5.7
0.46-OPC 3-FL	0.46	0.53	468	—	15	—	2.8

4.2.4 Isothermal Calorimetry

The rate of heat release and cumulative heat evolution was measured using an isothermal calorimeter in accordance with ASTM C1702-09 (38). Immediately after mixing, approximately 15 g of sample was transferred to a 22 mm diameter by 55 mm tall glass vial, sealed, and then placed into a chamber (maintained at 23 ± 0.1 °C) for approximately 60 h of testing. Prior to the data collection, the chamber was held in isothermal conditions for 45 min to establish an equilibrium baseline. Calorimetric studies were performed on each cementitious system at three w/p of 0.38, 0.42, and 0.46 at 23 °C and one w/p of 0.42 at 38 °C.

4.2.5 Chemical Shrinkage

The chemical shrinkage of each cementitious system was determined in accordance with ASTM C1608-07 (39). Samples of approximately 15 g were prepared and placed in 22 mm diameter by 55 mm tall glass vials in a controlled environment of 21 ± 0.5 °C. The samples

were covered with water, sealed with a rubber stopper fitted with a graduated capillary tube, and then filled until the water level was near the top mark on the capillary tube. The change in water level (and therefore volume) was recorded at specified intervals beginning at 6 hours after contact with water up to an age of one month.

4.2.6 Thermogravimetric Analysis and Differential Thermal Analysis

Thermogravimetric analysis and differential thermal analysis (TGA/DTA) was performed on the pastes to determine the chemically bound water (w_b) and the mass loss corresponding to the decomposition of $\text{Ca}(\text{OH})_2$ (labeled as CH_{loss}). The bound water can be understood as the amount of water that has taken part in the cement hydration reaction and was calculated from the mass loss between the temperatures of 160 to 1100 °C (35). Since the paste sample also consists of unhydrated cement, a correction to the calculations was performed by subtracting the mass loss associated with the decomposition of CaCO_3 , between the ranges of 600

to 780 °C, from the bound water. CH_{loss} was calculated within the temperatures of 440 to 520 °C, as this range is associated with the dehydroxylation of $Ca(OH)_2$.

The test was performed using a SDT-2960 simultaneous TGA/DTA device. After casting, pastes were transferred to a 22 mm diameter mold and sealed to cure at 23 ± 2 °C. At the desired curing ages (1, 2, 3, 7, 14, 28, and 90 days), the pastes were cut into 5 mm thick pieces and placed in methanol for one week to cease hydration. Before conducting the TGA/DTA testing, samples were oven dried for 24 h then ground into a fine powder. Samples of approximately 50 mg of the powder were placed in crucibles and put into testing chamber. The materials were then heated from 30 to 1100 °C at a rate of 20 °C/min. During the test, the chamber was purged with N_2 at 110 ml/min. Alumina powder was used as the reference.

4.2.7 X-ray Diffraction

X-ray diffraction (XRD) was conducted to determine the phase changes in pastes at different curing ages. By monitoring the formation of the carboaluminates, this testing technique allows the extent to which the limestone has participated in the hydration reactions to be evaluated (40). The tests were conducted with a Bruker D8 instrument with a $CuK\alpha$ source ($\lambda = 1.54 \text{ \AA}$) at 40 kV and 40 mA. Pastes at the desired curing age were cut into 5 mm thick pieces with a low-speed diamond saw and then loaded into the XRD equipment to perform measurements directly on the sample.

4.3 Results and Discussion

4.3.1 Calorimetry and Activation Energy Calculation

Calorimetry. The rate of heat evolution up to an age of 24 h and cumulative heat evolution up to 7 d are shown for each mixture in Figures 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, and 4.8. A comparison of OPC 1 and PLC 1 mixtures show that the initial 24 h of hydration of the PLC 1 mortars occur at a time that is not more than 1 h earlier than the OPC, with the 0.38-PLC 1 mixture experiencing the largest shift in initial hydration as seen in Figure 4.1a. It should be noted however that the secondary peak on the curve (commonly associated with the depletion of sulfates) is more pronounced in the PLC system. Inspection of the cumulative heat distribution of 0.42-PLC 1, seen in Figure 4.2b, shows an approximate reduction of -10% in heat released after 24 hours of age (the largest difference seen with most systems less than this difference). This data is normalized to the grams of binder in the sample, which includes the limestone which can be considered mostly inert and this would be consistent with dilution. In the following sections, this result will be discussed in terms of degree of hydration which will account for the dilution effect of the limestone. It should be noted that the 0.38 and 0.46-PLC 1's exhibited a greater

cumulative heat released after 24 hours of age despite the hidden effects of dilution in the data.

The rate of heat evolution for OPC 2 and PLC 2 mixtures with and without FA can be seen in Figure 4.3, while the cumulative heat evolution of these mixtures can be seen in Figure 4.4. A comparison of the rates of heat evolution of PLC 2 with OPC 2 shows that when FA is added to either OPC 2 or PLC 2, a general retardation of the system may be observed. Figure 4.5 shows that at w/p of 0.38 and 0.42 the cumulative heat evolution of the PLC 2 systems is nearly equivalent to that of the OPC 2. At a w/p of 0.46, the dilution in PLC 2 results in a reduction in the cumulative heat evolution of approximately 15%. The presence of FA in the PLC shows a similar retardation in the hydration as FA in the OPC, revealing no evidence to any nucleation effect that may improve the rate of hydration of the FA.

The rate of heat evolution for the OPC 3 and PLC 3 mixtures can be seen in Figure 4.5, with the cumulative heat released shown in Figure 4.6. Similar to PLC 1, during the initial 24 hours PLC 3 exhibits a shortened induction period by approximately 0.5 hours. After 24 hours, the cumulative heat released of the PLC 3 mixtures show an increase at all w/p, with a maximum increase of approximately 10% at 7 days. This is largely attributable to significant increase in fineness of the PLC 3 system discussed in the previous chapter. Again, it should be noted that the secondary peak associated with the depletion of sulfates is more prominent in the PLC systems. This may be attributable to the stabilization of monocarbonate instead of monosulfate due to the presence of limestone during hydration (41).

The rate of heat evolution for OPC 4, OPC 4-CL, and OPC 4-FL can be seen in Figure 4.7, with the cumulative heat released for these materials shown in Figure 4.8. The addition of FL shortened the induction period by approximately 1 hour while the CL had little effect on the length of induction period. This difference is likely attributable to whether the limestone particle could provide enough surface area to accelerate C-S-H formation. In general, after 24 hours a reduction of cumulative heat released in the blended limestone systems is observed at all w/p, with the difference between limestone particle sizes being negligible.

The previous section presented data on the hydration of cementitious systems containing ground limestone. It was shown that the interground PLC mortars (PLC1, PLC 2, PLC 3, and PLC 2-FA) release slightly less (no more than 10%) or in some cases more heat than the corresponding OPC mortars after 7 days curing. The heat loss due to dilution is not observed and this indicates additional reactions in the PLC system. When the limestone was blended with the cement (OPC 4-CL and OPC 4-FL), the heat release of the limestone systems showed a reduction of as much as -15%, indicating that these systems which is consistent with dilution. A common occurrence in all of the mixtures containing limestone were the pronounced secondary peaks, suggesting that the sulfate levels of each system may be altered with limestone addition. This may be

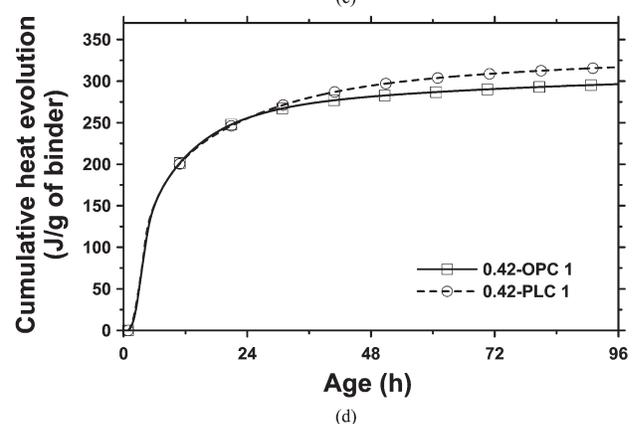
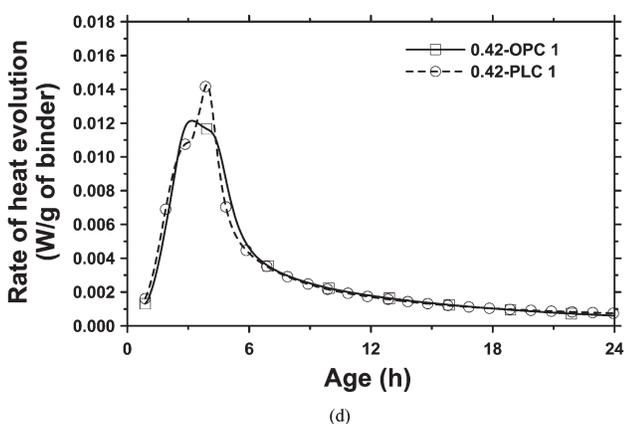
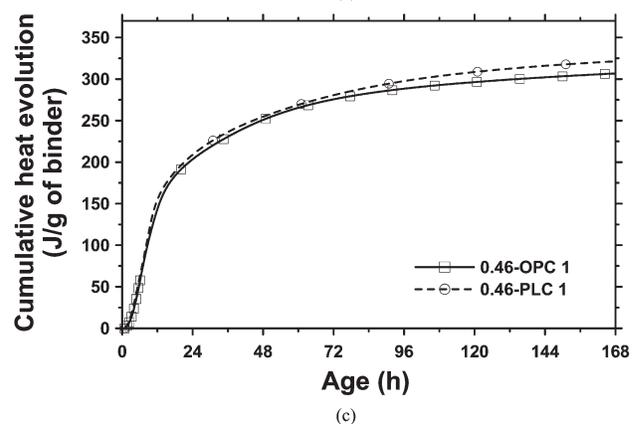
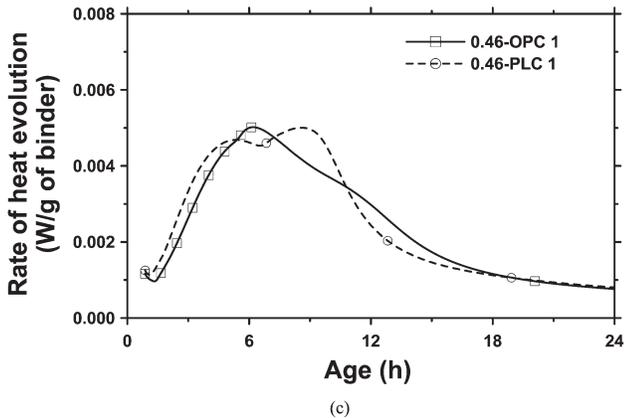
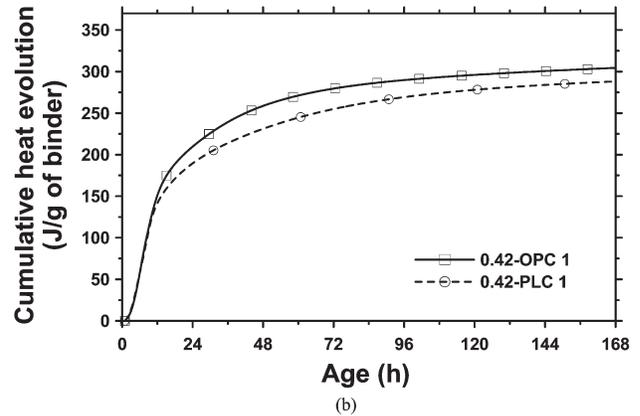
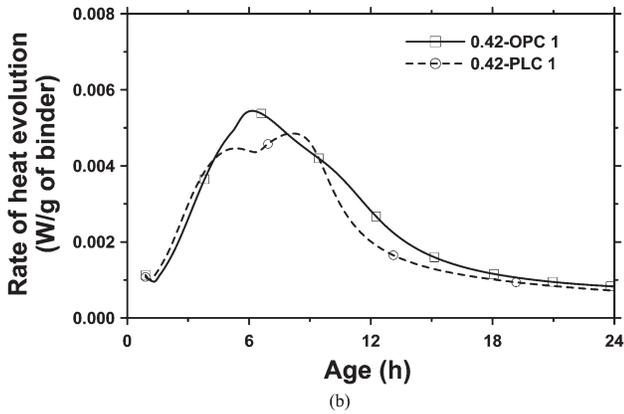
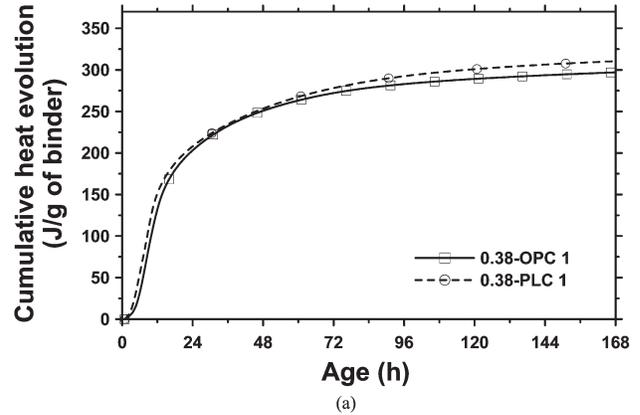
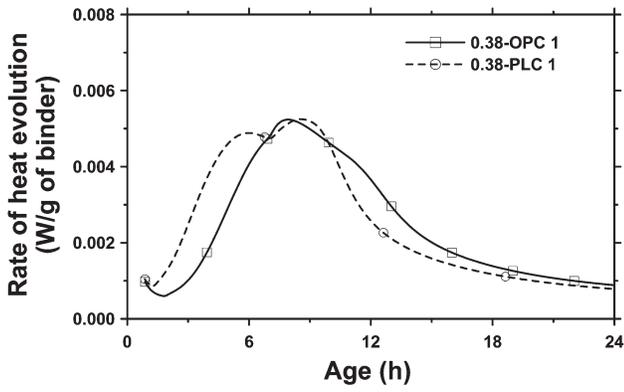


Figure 4.1 The rate of heat evolution of (a) 0.38-OPC/PLC 1 at 23 °C, (b) 0.42-OPC/PLC 1 at 23 °C, (c) 0.46-OPC/PLC 1 at 23 °C, and (d) 0.42-OPC/PLC 1 mortars at 38 °C.

Figure 4.2 The cumulative heat evolution of (a) 0.38-OPC/PLC 1 at 23 °C, (b) 0.42-OPC/PLC 1 at 23 °C, (c) 0.46-OPC/PLC 1 at 23 °C, and (d) 0.42-OPC/PLC 1 mortars at 38 °C.

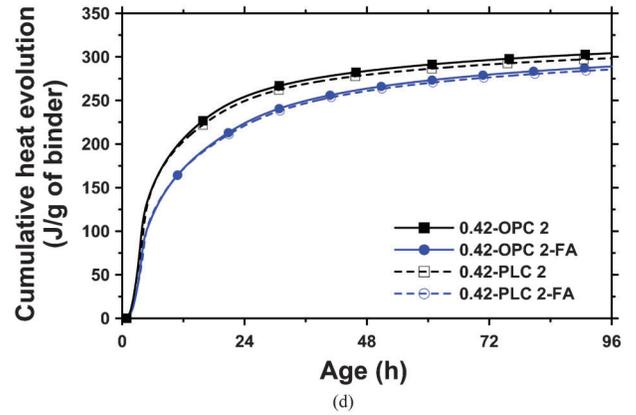
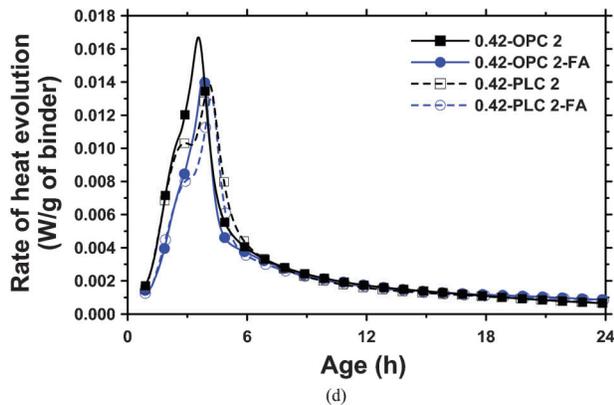
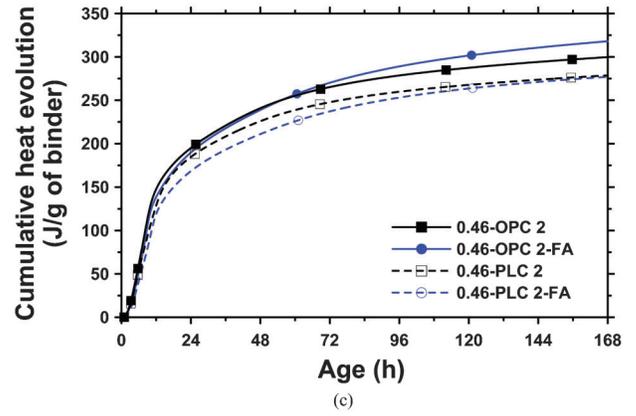
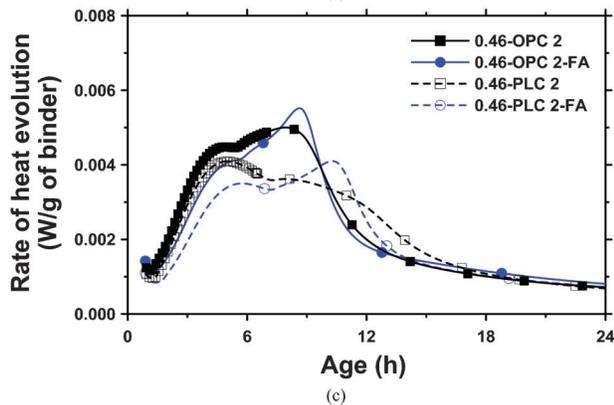
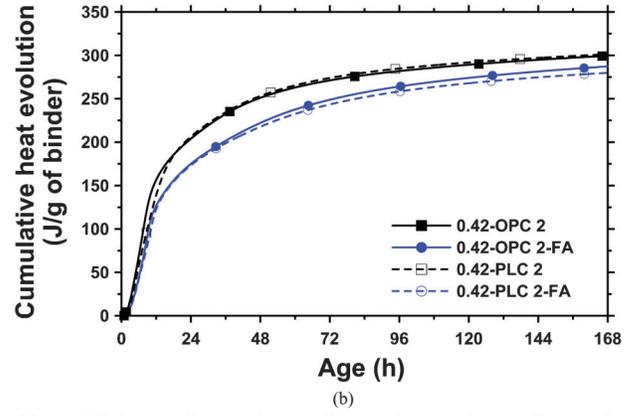
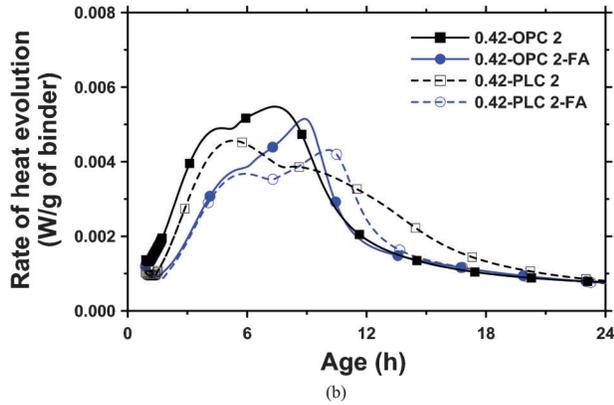
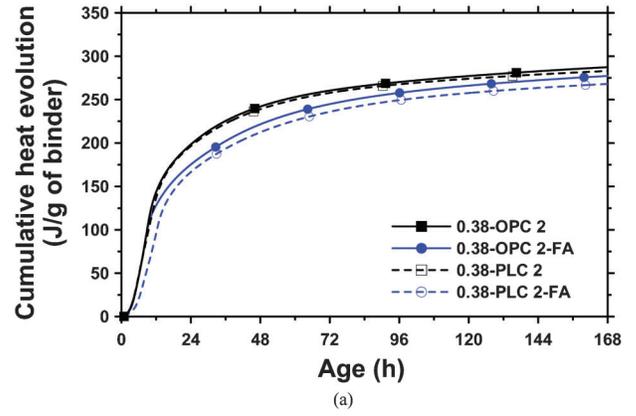
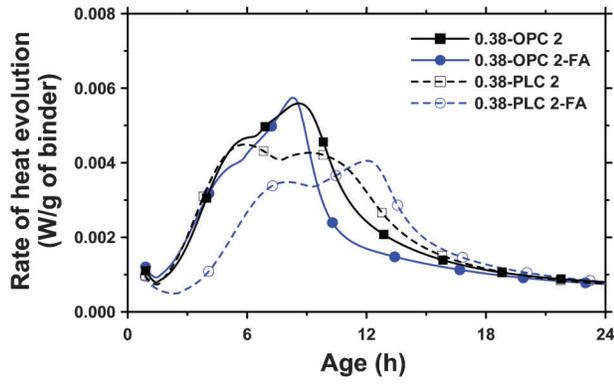
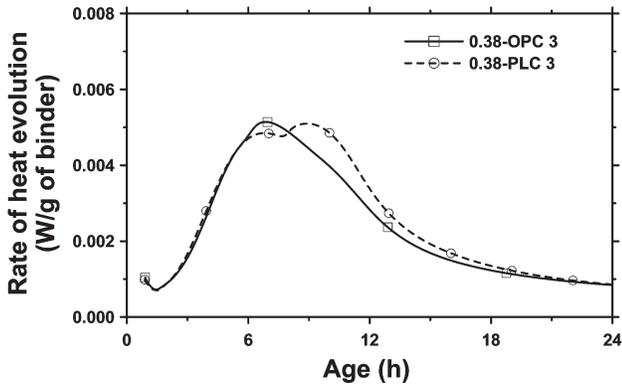
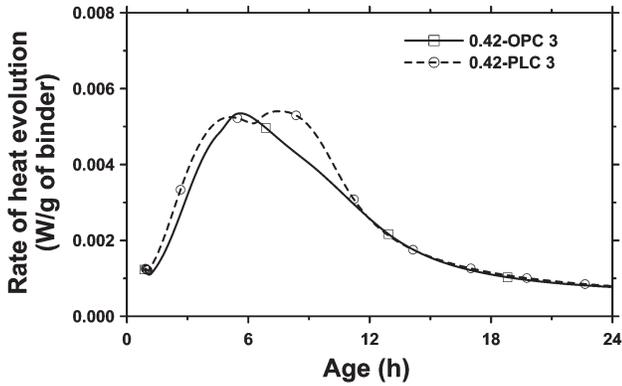


Figure 4.3 The rate of heat evolution of (a) 0.38-OPC/PLC 2 and 0.38-OPC/PLC 2-FA at 23 °C, (b) 0.42-OPC/PLC 2 and 0.42-OPC/PLC 2-FA at 23 °C, (c) 0.46-OPC/PLC 2 and 0.46-OPC/PLC 2-FA at 23 °C, and (d) 0.42-OPC/PLC 2 and 0.42-OPC/PLC 2-FA mortars at 38 °C.

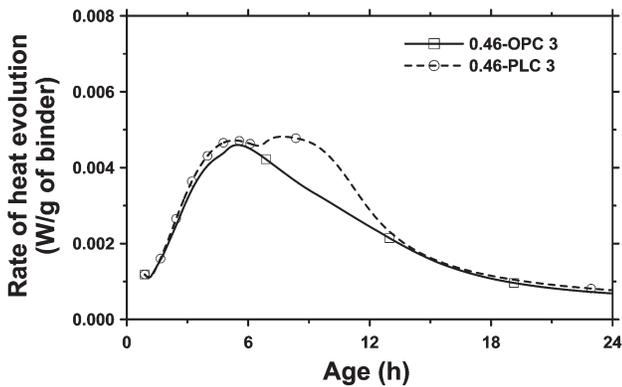
Figure 4.4 The cumulative heat evolution of (a) 0.38-OPC/PLC 2 and 0.38-OPC/PLC 2-FA at 23 °C, (b) 0.42-OPC/PLC 2 and 0.42-OPC/PLC 2-FA at 23 °C, (c) 0.46-OPC/PLC 2 and 0.46-OPC/PLC 2-FA at 23 °C, and (d) 0.42-OPC/PLC 2 and 0.42-OPC/PLC 2-FA mortars at 38 °C.



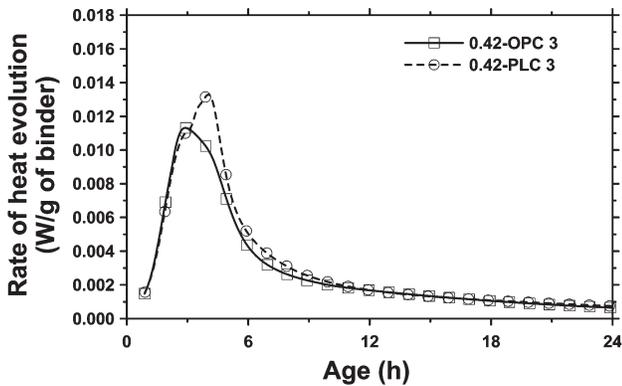
(a)



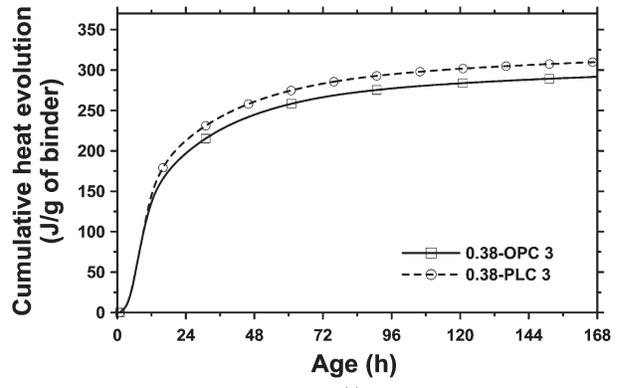
(b)



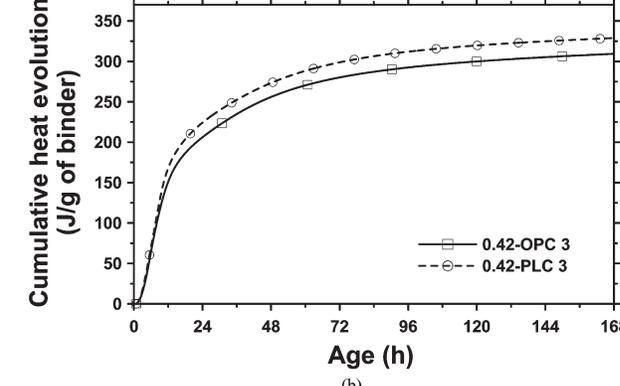
(c)



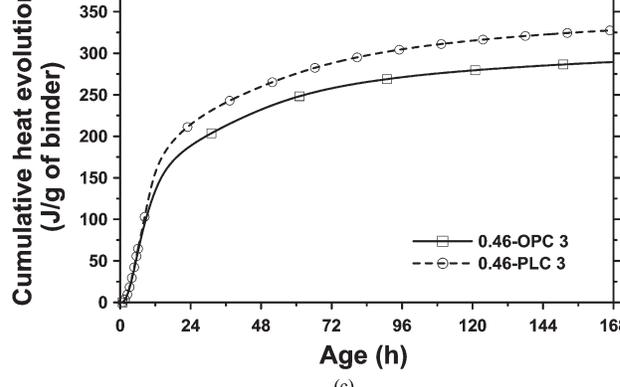
(d)



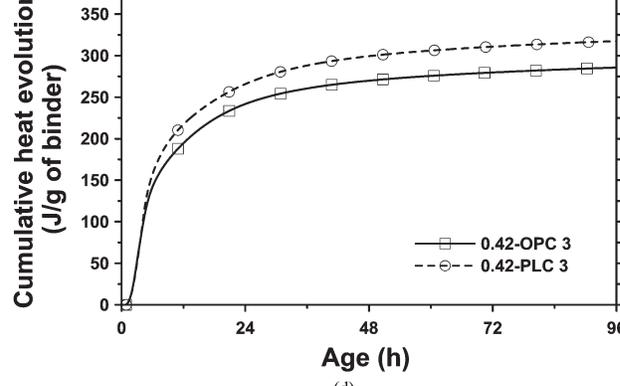
(a)



(b)



(c)



(d)

Figure 4.5 The rate of heat evolution of (a) 0.38-OPC/PLC 3 at 23 °C, (b) 0.42-OPC/PLC 3 at 23 °C, (c) 0.46-OPC/PLC 3 at 23 °C, and (d) 0.42-OPC/PLC 3 mortars at 38 °C.

Figure 4.6 The cumulative heat evolution of (a) 0.38-OPC/PLC 3 at 23 °C, (b) 0.42-OPC/PLC 3 at 23 °C, (c) 0.46-OPC/PLC 3 at 23 °C, and (d) 0.42-OPC/PLC 3 mortars at 38 °C.

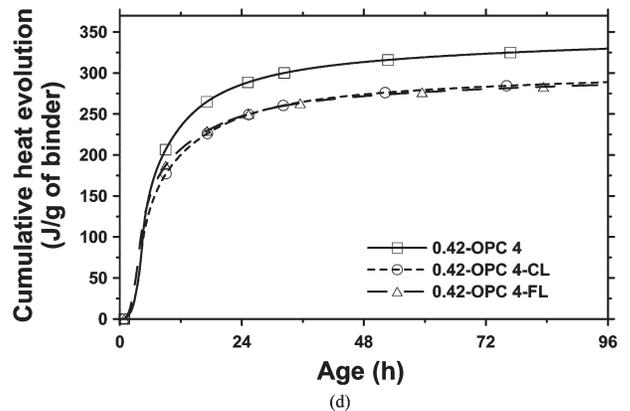
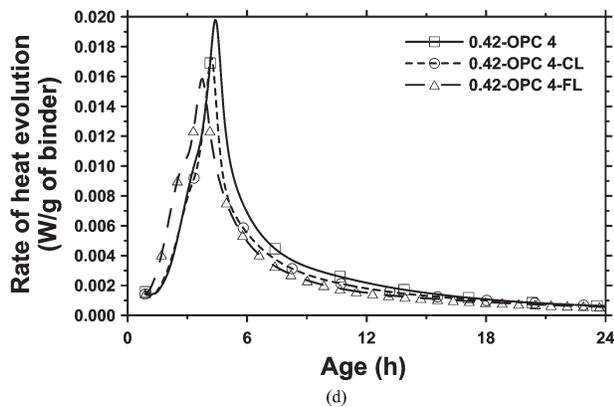
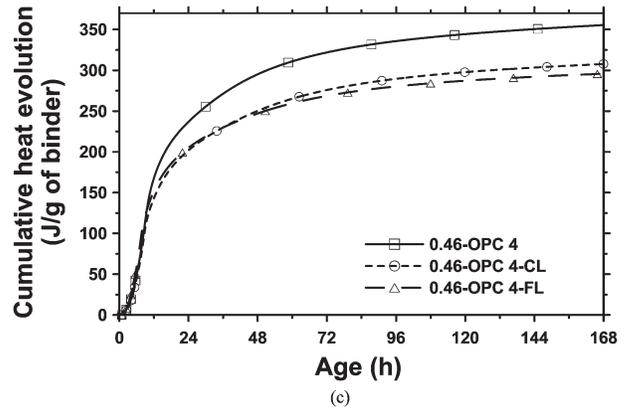
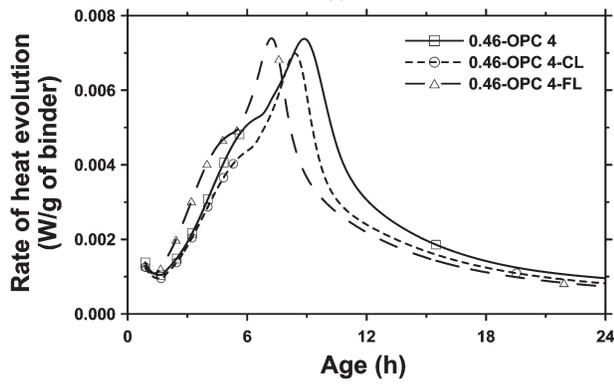
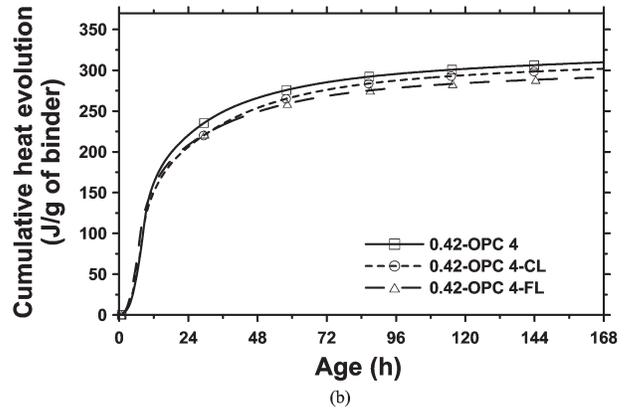
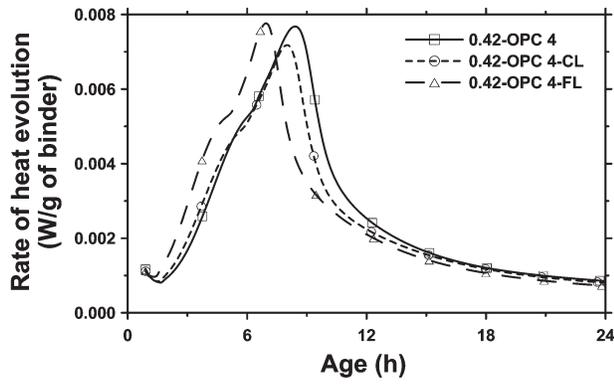
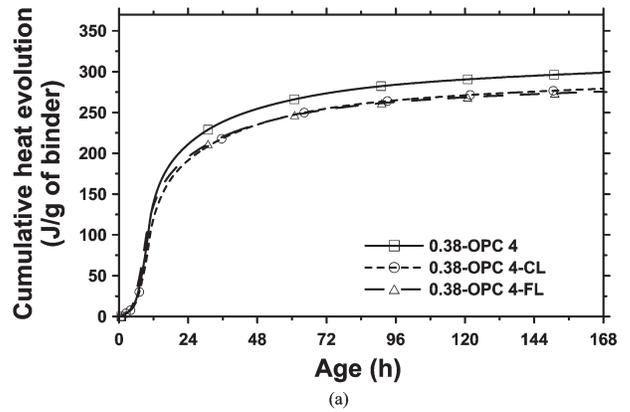
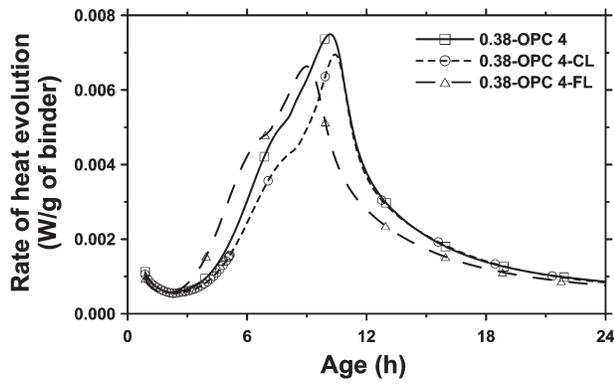


Figure 4.7 The rate of heat evolution of (a) 0.38-OPC 4, 0.38-OPC 4-CL, and 0.38 OPC 4-FL at 23 °C, (b) 0.42-OPC 4, 0.42-OPC 4-CL, and 0.42 OPC 4-FL at 23 °C, (c) 0.46-OPC 4, 0.46-OPC 4-CL, and 0.46 OPC 4-FL at 23 °C, and (d) 0.42-OPC 4, 0.42-OPC 4-CL, and 0.42 OPC 4-FL at 38 °C.

Figure 4.8 The cumulative heat evolution of (a) 0.38-OPC 4, 0.38-OPC 4-CL, and 0.38 OPC 4-FL at 23 °C, (b) 0.42-OPC 4, 0.42-OPC 4-CL, and 0.42 OPC 4-FL at 23 °C, (c) 0.46-OPC 4, 0.46-OPC 4-CL, and 0.46 OPC 4-FL at 23 °C, and (d) 0.42-OPC 4, 0.42-OPC 4-CL, and 0.42 OPC 4-FL at 38 °C.

attributable to the stabilization of monocarbonate in the presence of limestone (41) which may change the sulfate demand.

Maximum heat released (Q_∞) calculation. Using the calorimetry data, the maximum heat released (Q_∞) was calculated to derive the degree of hydration (DOH), defined as the heat at any given time divided by the maximum heat released (Q / Q_∞), as one of the necessary steps to calculate the activation energy (E_a) (42,43). In this calculation, the limestone is considered as inert (44,45). Q_∞ was calculated using Equation 1 (46).

$$Q_\infty = 500P_{C_3S} + 260P_{C_2S} + 866P_{C_3A} + 420P_{C_4AF} + 624P_{SO_3} + 1186P_{FreeCaO} + 850P_{MgO} \quad (1)$$

If supplementary cementitious materials, herein fly ash, were used then:

$$Q = Q_\infty P_{cem} + 1800P_{FA}CaO \quad (2)$$

where P_i denotes the proportion of the i -th composition by weight. $P_{FA}CaO$ is the ratio of CaO mass in fly ash to total fly ash mass. The calculated results are shown in Table 4.3.

Degree of hydration. Using the results from the previous two sections, the DOH was able to be assessed for each mixture at a w/p of 0.42 as shown in Figure 4.9. A comparison of the PLC systems with the blended limestone systems is made. Each of the PLCs investigated met or exceeded the DOH of the reference OPCs during the first seven days of hydration, with PLC 2 and PLC 3 showing an increase greater than 5%. In contrast to this, the rate of hydration in the blended limestone cements is dependent on the fineness of the limestone particles. The 0.42-OPC 4-CL mixture demonstrated an approximate reduction of 10% in the DOH, but increasing the fineness of the limestone (0.42-OPC 4-FL) resulted in equivalent DOH as the reference mixture. This data suggests that a higher

TABLE 4.3
 Q_∞ as calculated by cement composition

Specimen	Q_∞ (J/g)
0.42-OPC 1	459
0.42-PLC 1	418
0.42-OPC 2	416
0.42-OPC 2-FA	421
0.42-PLC 2	389
0.42-PLC 2-FA	421
0.42-OPC 3	426
0.42-PLC 3	392
0.42-OPC 4	430
0.42-OPC 4-FL	410
0.42-OPC 4-CL	495

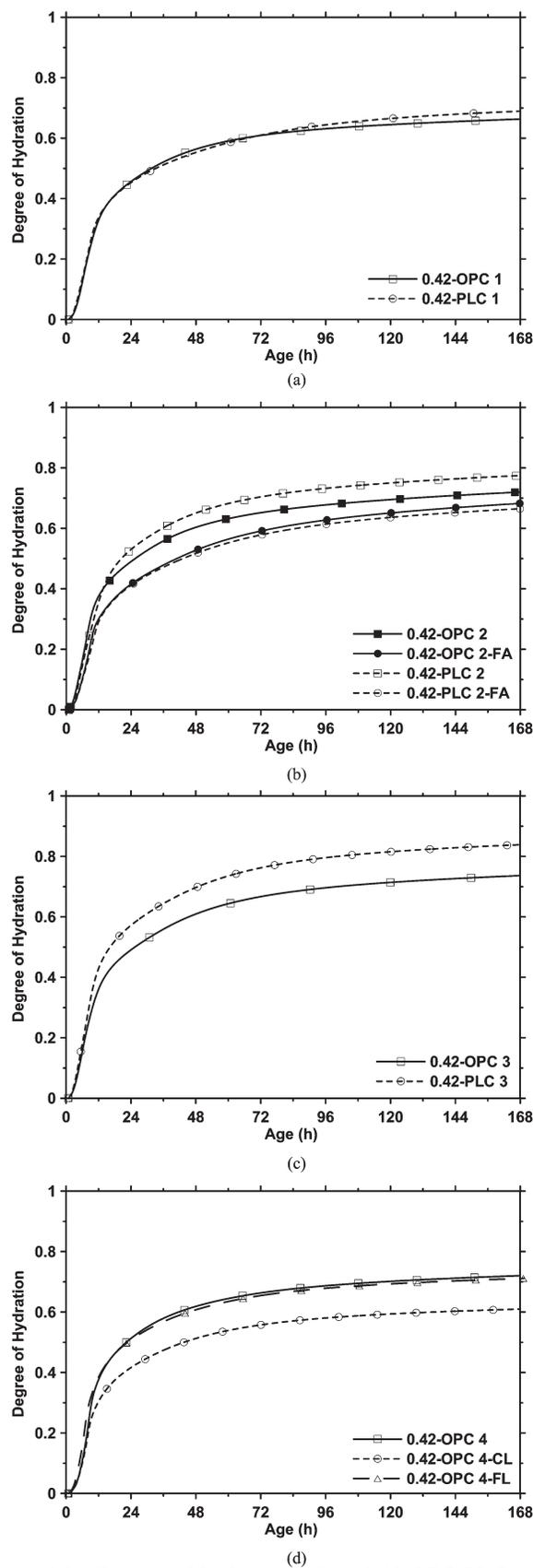


Figure 4.9 Degree of hydration of (a) 0.42-OPC/PLC 1, (b) 0.42-OPC/PLC 2 with and without fly ash, (c) 0.42-OPC/PLC 3, and (d) 0.42-OPC 4, 0.42-OPC 4-CL, and 0.42-OPC 4-FL.

DOH may be achievable if even finer (mean particle size less than 1.3 μm) limestone particles were blended with the cement. The presence of fly ash in the mixtures resulted in a general reduction in DOH due to the slower nature of the pozzolanic reaction while the additional replacement of limestone resulted in a similar DOH during the first seven days of hydration.

Calculation of activation energy. The activation energy (E_a) of all specimens was calculated so that the effects of limestone on maturity models could be evaluated. The E_a of each mixture at a w/p of 0.42 is shown as a function of DOH in Figure 4.10, with average values listed in Table 4.4. The average value was calculated with a DOH within the range of 0.1 to 0.5 with the exception of PLC1 and OPC 4 where the range was limited to 0.1 to 0.35. The results show that the PLC and OPC have similar activation energies and therefore specific changes are not needed for use with the maturity method.

4.3.2 Chemical Shrinkage

Chemical shrinkage is defined as the volume reduction associated with the hydration reaction of cementitious systems. When monitored over a period of time, the chemical shrinkage can be used to study the relative hydration of these systems. In this section, chemical shrinkage results up to 1 month of age are presented in Figures 4.11, 4.12, 4.13, and 4.14. In each figure, the results are normalized per gram of binder in part (a) and per gram of cement in part (b). Normalizing per gram of cement allows for a direct comparison of the degree of hydration of the clinker in limestone systems with their OPC references while normalizing per gram of binder includes the effect of dilution in the limestone systems when comparing to their OPC references.

Figure 4.11a shows a reduction of approximately 10% for PLC 1 at an age of 1 month. When the data is normalized by the mass of cement (Figure 4.11b), this difference was reduced to 5.5%. These results suggest a slight reduction in the formation of hydration products in the PLC 1 system.

Figure 4.12 shows the chemical shrinkage of the OPC 2 and PLC 2 systems with and without FA. When this data is normalized by mass of binder, an increase in chemical shrinkage in PLC 2 is seen after 1 day of age, with a maximum increase of approximately 9% at one month, suggesting that the cement was ground finely enough to overcome the effects of dilution. When assessing the effects of replacing a portion of the system with fly ash, it is better to draw comparisons by gram of binder, as the fly ash in the system is not an inert filler. Figure 4.12a shows an increase of 8% in chemical shrinkage for the systems with FA after approximately two days of hydration. Figure 4.12b suggests that the presence of limestone in the PLC 2-FA system results in a slight increase in hydration products, inferring that the limestone presence of limestone is able increase the

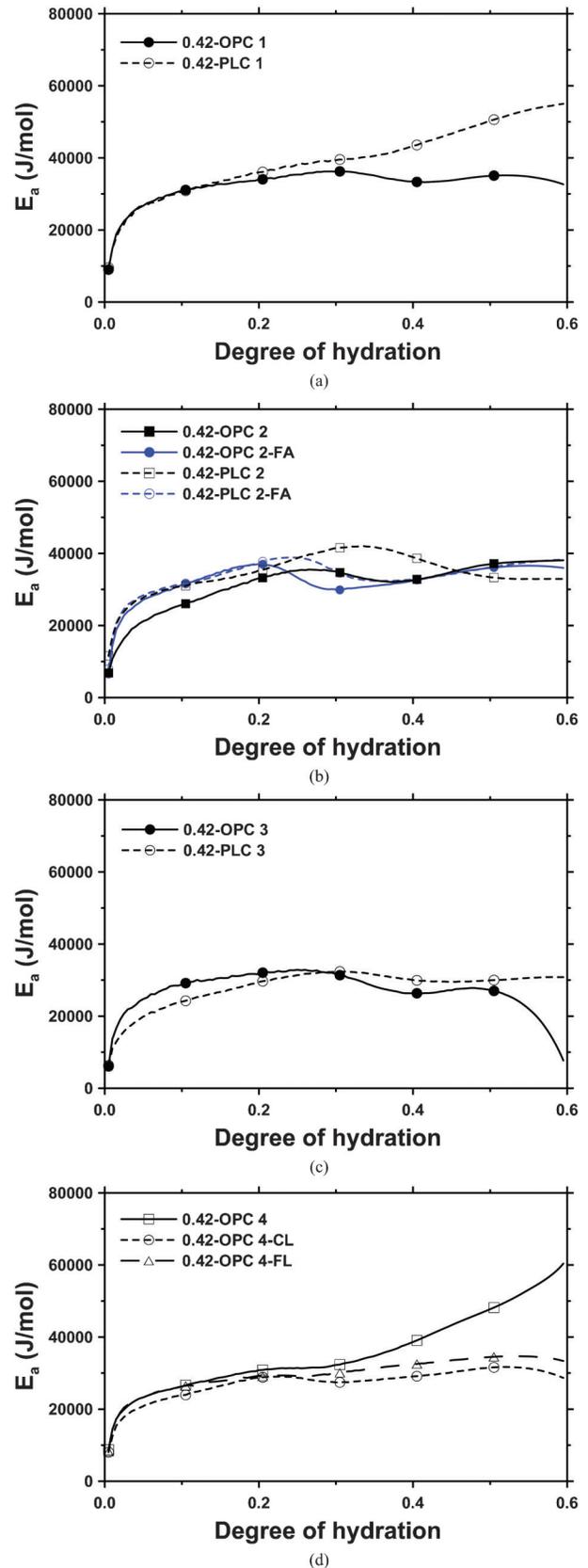


Figure 4.10 Evolution of apparent activation energy for (a) 0.42-OPC/PLC-1, (b) 0.42-OPC/PLC-2 and 0.42-OPC/PLC-2-FA, (c) 0.42-OPC/PLC-3, and (d) 0.42-OPC-4, 0.42-OPC-4-CL, and 0.42-OPC-4-FL.

TABLE 4.4
Average activation energy (E_a)

Specimen	E_a (J/mol)
0.42-OPC 1	34200
0.42-PLC 1	42400
0.42-OPC 2	33900
0.42-OPC 2-FA	33900
0.42-PLC 2	36200
0.42-PLC 2-FA	35300
0.42-OPC 3	27600
0.42-PLC 3	29800
0.42-OPC 4	38400
0.42-OPC 4-CL	28700
0.42-OPC 4-FL	31200

hydration of the blended cement-fly ash system enough to not experience effects of dilution.

Figure 4.13a shows that the difference in the measured chemical shrinkage between OPC 3 and PLC 3 mortars is insignificant over the first 1 month.

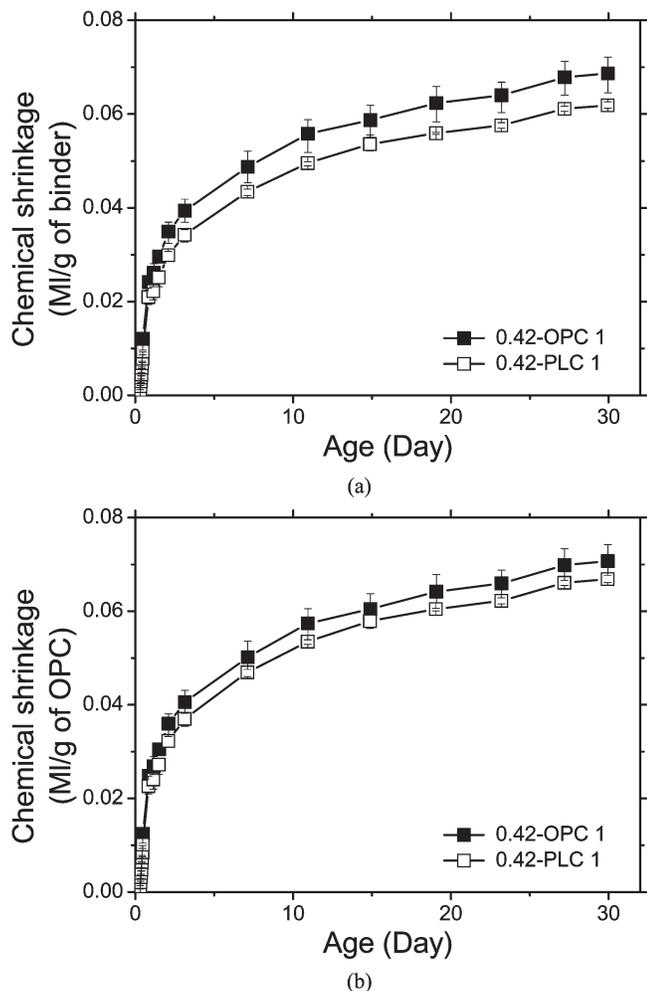


Figure 4.11 Chemical shrinkage normalized by (a) grams of binder and (b) grams of cement of 0.42-OPC/PLC-1 mortars up to 30 days.

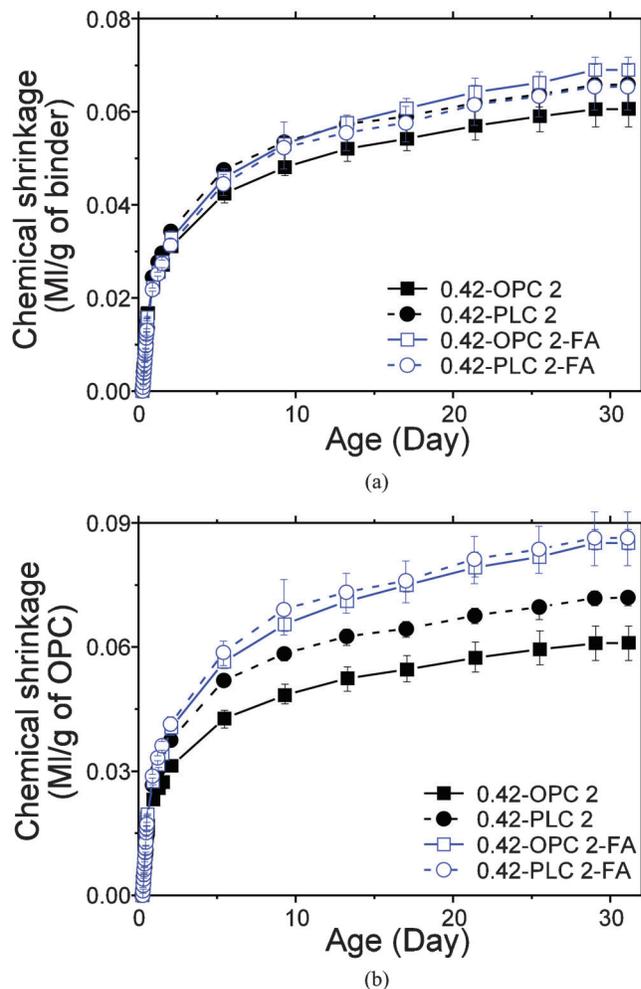


Figure 4.12 Chemical shrinkage normalized by (a) grams of binder and (b) grams of cement of 0.42-OPC/PLC-2 and 0.42-OPC/PLC-2-FA mortars up to 30 days.

When the data is normalized per mass of cement (Figure 4.13b), the chemical shrinkage of PLC 3 is shown to have increased by 6% compared OPC 3 at one month. These results suggest a slight increase in the formation of hydration products in PLC 3 (possibly carboaluminates) where the finer ground system has overcome the dilution due to the presence of limestone.

Figure 4.14 shows the chemical shrinkage of the blended limestone cement systems. In Figure 4.14a, the difference between OPC 4 and the two blended limestone systems is relatively insignificant over the first 1 month. Figure 4.14b shows an increase in hydration in the blended limestone cements. It should be noted that the size of limestone seems not to affect the overall degree of hydration of the system significantly, which corresponds with the calorimetry data shown previously.

In the previous section, the chemical shrinkage of each limestone system was shown to be similar to, or greater than, that of corresponding OPC mortars (from a 0% to 10% increase). In all cement systems with the

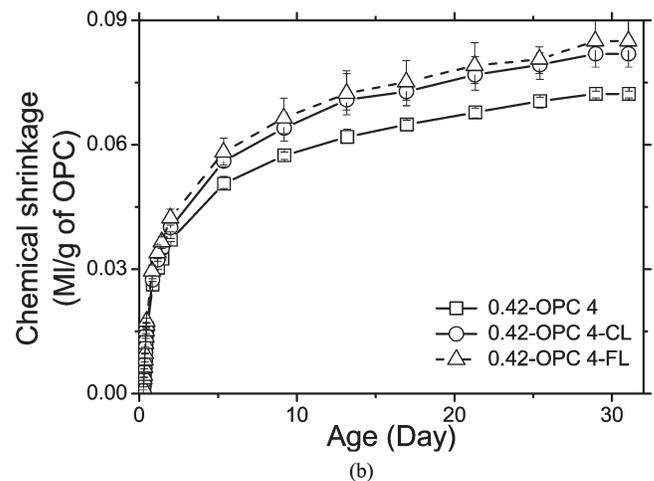
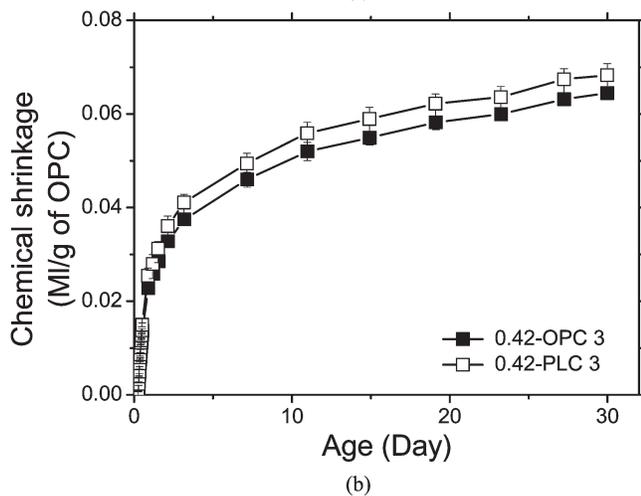
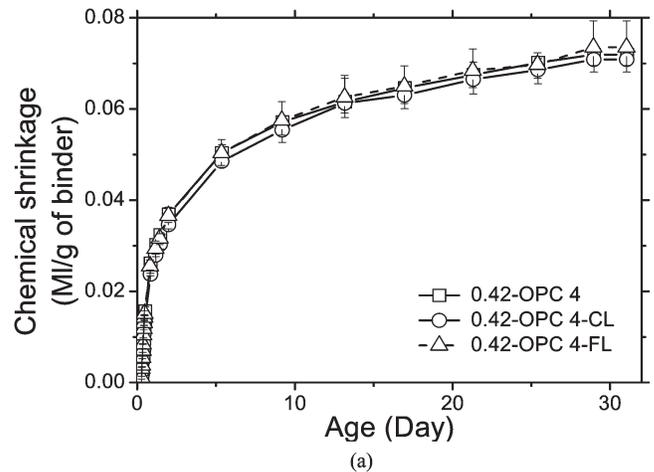
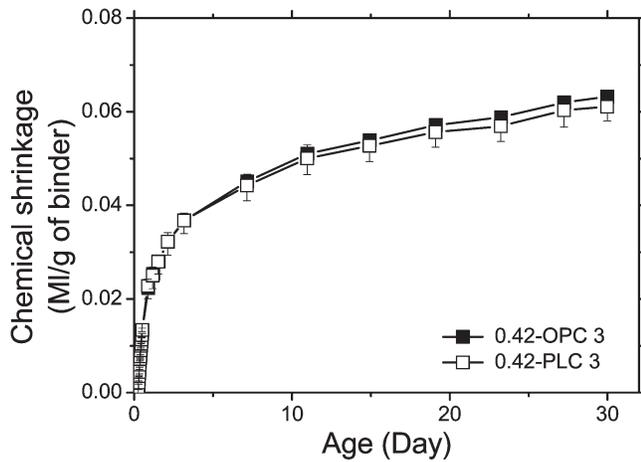


Figure 4.13 Chemical shrinkage normalized by (a) grams of binder and (b) grams of cement of 0.42-OPC/PLC-3 mortars up to 30 days.

Figure 4.14 Chemical shrinkage normalized by (a) grams of binder and (b) grams of cement of 0.42-OPC-4, 0.42-OPC-4-CL, and 0.42-OPC-4-FL mortars up to 30 days.

exception of OCP 1/PLC 1, this indicates a similar level of hydration or an increase in the degree of hydration for the PLC mortars in comparison to the OPCs.

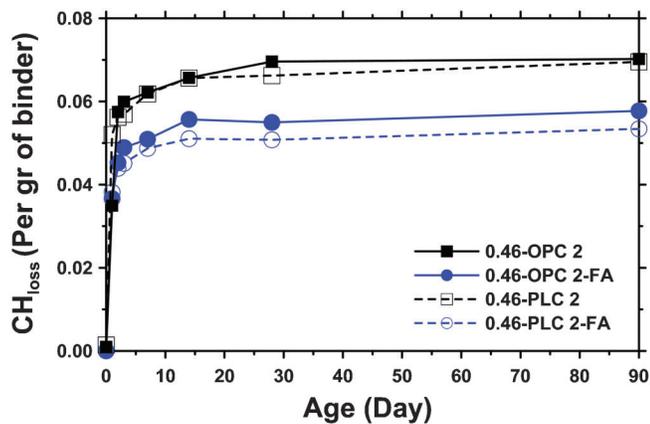
4.3.3 Thermogravimetric Analysis and Differential Thermal Analysis

DTA/TGA analyses were carried out on the 0.46-OPC 2, 0.46-PLC 2, 0.46-OPC 2-FA, 0.46-OPC 2-FA, and 0.46-OPC 4 mixtures to determine the amount of calcium hydroxide (CH) that forms and the quantity of chemically bound water over 90 days of hydration. The results are shown in Figure 4.15 and Figure 4.16, being normalized by gram of binder in part (a) and by gram of cement in part (b) of each figure. Comparing OPC 2 with PLC 2 shows that the CH content per mass of binder decreases when limestone is present either with or without fly ash. When normalized to the mass of cement, it is shown that more CH is formed in the PLC 2 mixture, suggesting that a higher degree of hydration has been reached, which is consistent with the calorimetry and chemical shrinkage results. In the

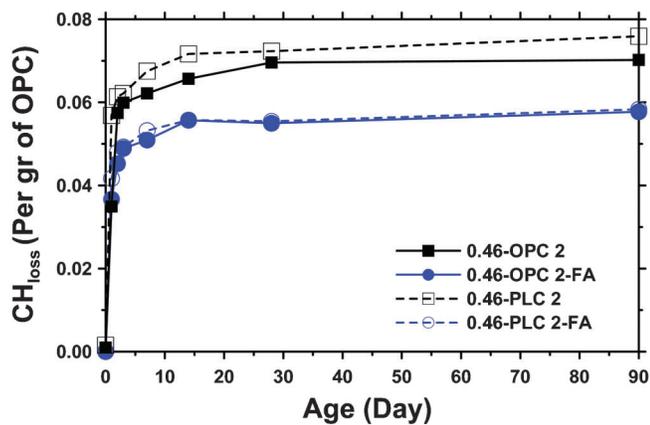
OPC 2-FA and PLC 2-FA mixtures, the presence of fly ash leads to the consumption of CH due to the pozzolanic reaction of the FA, as seen in Figure 4.15. It should be noted that the fly ash may also react with limestone either directly or in-directly (especially at later ages), leading to a potential reduction in the effects of dilution that may be expected in the PLC systems.

In the OPC 4-CL and OPC 4-FL mixtures, it can be noticed that the effects of dilution are not overcome by the nucleation and/or particle packing effects by comparing Figure 4.16a with Figure 4.16b. In part (b) of the figure the blended limestone systems suggest an increase in formation of CH, however in part (a) they show a reduction of more than 6% after one month. It can also be noticed from this data that almost no difference in the formation of hydration products was found with varying particle sizes of limestone. This may suggest that the presence of the limestone encouraging the precipitation of CH (nucleation) may be more significant than the effects of enhanced particle packing from the limestone.

The ultimate quantity of bound water (w_b) is shown in Figure 4.17 and Figure 4.18. The w_b of the 0.46-PLC



(a)



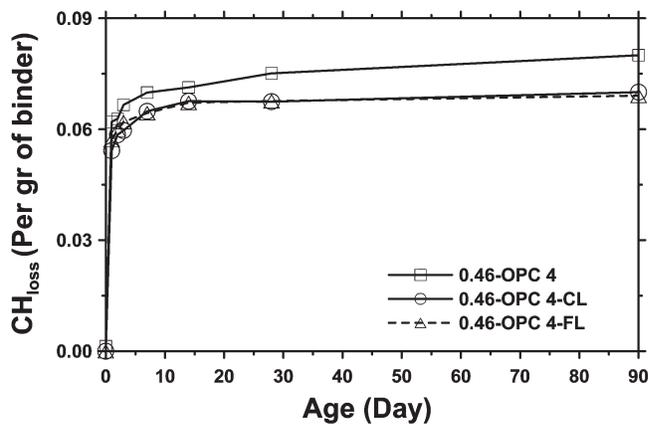
(b)

Figure 4.15 Calcium hydroxide loss normalized by (a) gram of binder and (b) gram of cement for 0.46-OPC/PLC 2 with and without fly ash.

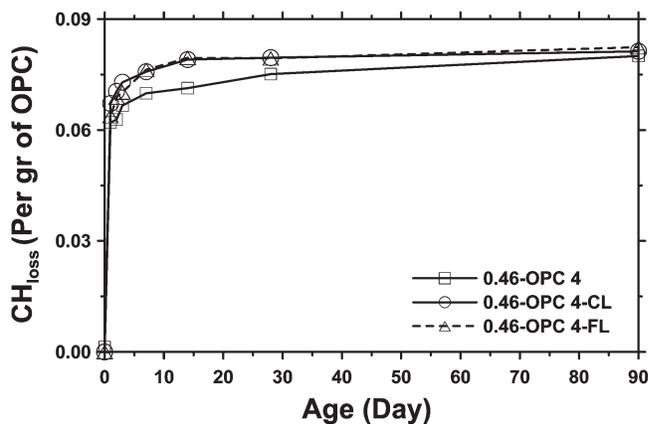
2 and 0.46-OPC 2-FA mixtures were found to be slightly greater than their references at all ages when normalized per gram of binder. This is consistent with the findings the chemical shrinkage data. In Figure 4.18 it can be observed that the blended limestone mixtures have a higher quantity of w_b than the 0.46-OPC 4 mixture up two weeks of age, after which they have the same or less bound water. This may suggest that the hydration of the 0.46-OPC 4-CL and 0.46-OPC 4-FL mixtures is inhibited by the effects of dilution after approximately two weeks.

4.3.4 X-ray Diffraction

The XRD characterization of the 0.46-OPC 2, 0.46-PLC 2, 0.46-OPC 2-FA, 0.46-OPC 2-FA, and 0.46-OPC 4 mixtures at ages up to 90 days is shown in Figures 4.19, 4.20, and 4.21. The results show that a primary phase exists at an angle of $2\theta = 11.7^\circ$, representing a distinct presence of monocarbonate in all cementitious systems containing limestone. This suggests that a small portion of the limestone is participating in the hydration reaction with the aluminate phase, especially at later ages of 28 days or more. The presence of fly ash enables the formation



(a)



(b)

Figure 4.16 Calcium hydroxide loss normalized by (a) gram of binder and (b) gram of cement for 0.46-OPC 4, 0.46-OPC 4-CL, and 0.46-OPC 4-FL.

of significantly more monocarbonate, presenting a much higher peak of the monocarbonate phase in Figure 4.20. In addition to the presence of monocarbonate, the hemicarbonate phase was also observed however due to the resolution of XRD spectra, the peak of hemicarbonate phase is relatively low.

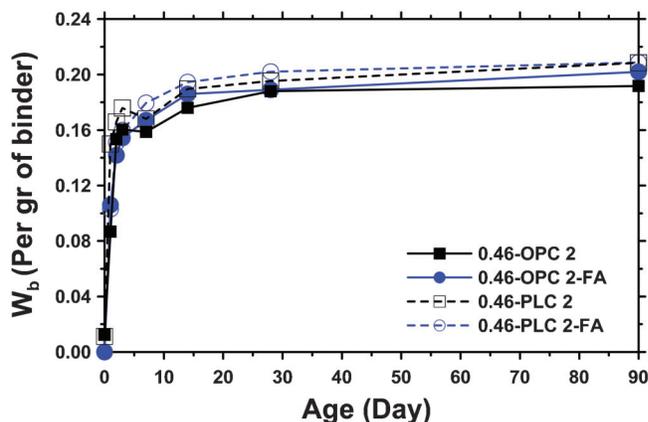


Figure 4.17 The quantity of bound water in 0.46-OPC/PLC 2 with and without fly ash.

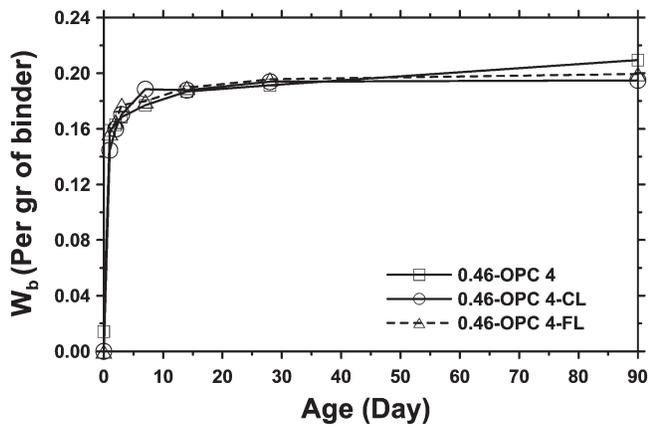


Figure 4.18 The quantity of bound water in 0.46-OPC 4, 0.46-OPC 4-CL, and 0.46-OPC 4-FL.

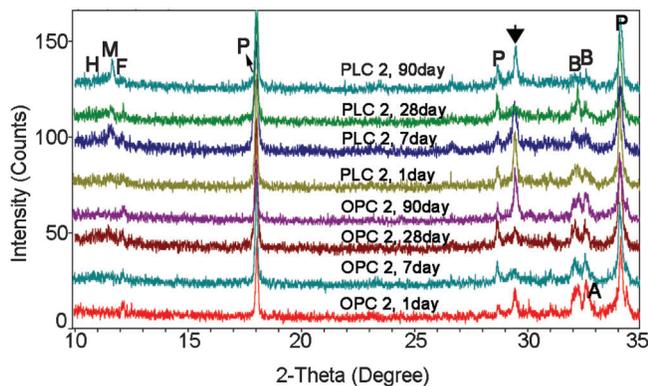


Figure 4.19 XRD of OPC 2 and PLC 2 pastes at ages up to 90 days. A = C_3S (alite), B = C_2S (belite), P = CH (portlandite), F = C_4AF (ferrite), M = monocarbonate, H = hemicarbonate, Arrow: $CaCO_3$ (calcite).

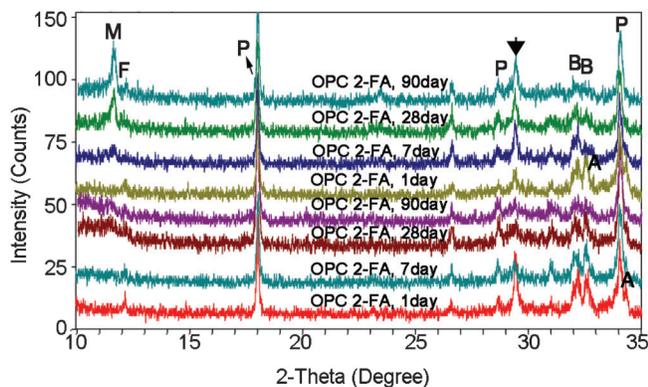


Figure 4.20 XRD of OPC 2-FA and PLC 2-FA pastes at ages up to 90 days. A = C_3S (alite), B = C_2S (belite), P = CH (portlandite), F = C_4AF (ferrite), M = monocarbonate, H = hemicarbonate, Arrow: $CaCO_3$ (calcite).

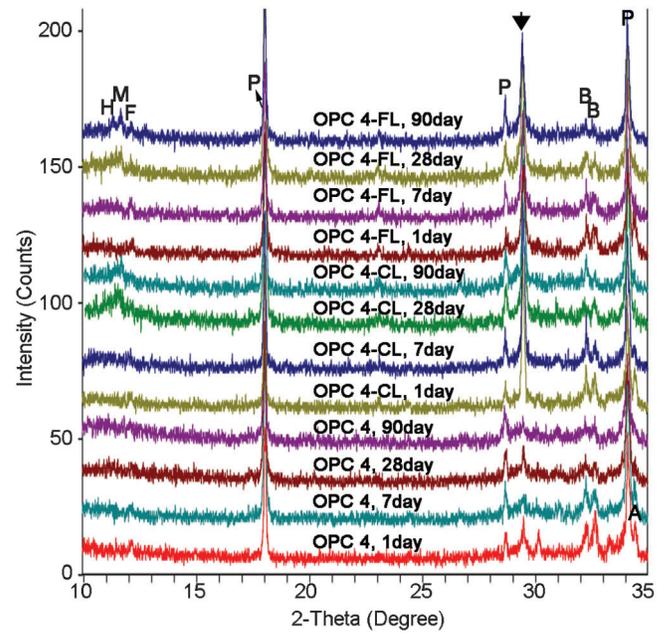


Figure 4.21 XRD of OPC 4, OPC 4-CL, and OPC 4-FL pastes at ages up to 90 days. A = C_3S (alite), B = C_2S (belite), P = CH (portlandite), F = C_4AF (ferrite), M = monocarbonate, H = Hemicarbonate, Arrow: $CaCO_3$ (calcite).

4.4 Summary and Conclusions

This chapter discussed the hydration reaction of cementitious systems containing limestone. The observations made here can be summarized:

- PLC mortars typically exhibit a greater heat release than the OPC counterparts after 7 days of curing, corresponding to a degree of hydration that met or exceeded the reference mortars. The blended limestone systems (OPC 4-CL and OPC 4-FL) both exhibited lower amounts of heat released at early ages, corresponding to a similar degree of hydration for the FL system and a 10% reduction in the CL system in comparison to OPC 4.
- PLC mortars exhibited similar, albeit slightly higher, average activation energies compared to the corresponding OPCs.
- The chemical shrinkage (when normalized to the cement content) of PLCs (with the exception of PLC 1) is similar or greater than that of corresponding OPC mortars (increase of up to 10%), indicating a higher level of hydration in the PLC mortars compared to the OPCs. The chemical shrinkage of the blended limestone systems also showed an increase in chemical shrinkage, with negligible difference due to the size of the limestone particles.
- TGA/DTA analysis showed that (when normalized to the cement content) the limestone systems had a greater volume of CH compared to the corresponding OPCs, suggesting the formation of more hydration products.
- All cementitious systems containing limestone showed a stronger monocarbonate peak than the corresponding OPCs, especially at ages of 28 days or more. Additionally, the presence of fly ash resulted in the formation of significantly more monocarbonate in the PLC pastes.

5. EVALUATION OF THE MECHANICAL PROPERTIES OF SYSTEMS CONTAINING LIMESTONE ADDITIONS

5.1 Introduction

The intent of introducing portland limestone cements (PLCs) under ASTM C595 (i.e., North America) is to address the growing concerns of sustainability in cement and concrete production. PLCs are intended to provide a direct replacement for ASTM C150 Type I/II ordinary portland cements (OPCs) that achieves similar performance while reducing clinker content. This chapter presents results on the mechanical properties of these PLCs as assessed through standardized testing methods, while evaluating the following five comparisons:

1. OPC versus PLC
2. Interground limestone cements (PLCs) versus blended limestone cements
3. Varying water-to-powder ratios (w/p) of 0.38, 0.42, and 0.46 (representing the upper, middle, and lower bounds as permissible under INDOT specifications)
4. Effect of particle size of ground limestone used in blended limestone cement systems
5. Effect of including fly ash in OPC versus PLC cement systems

The mechanical properties that were tested include the time of set (TOS), compressive strength, static modulus of elasticity (Young's), flexural strength, free shrinkage in sealed and drying conditions, and restrained shrinkage behavior. In the interest of a systematic treatment of each underlying variables being tested, the discussion of results from each test will address each of these variables and will be listed accordingly by number.

5.2 Materials and Methods

5.2.1 Materials

Three commercially produced, ASTM C150 Type I/II (I) ordinary portland cements (OPC 1-3) with complimentary ASTM C595 Type IL (16) portland limestone cements (PLC 1-3) containing 10% to 15% replacement of cement by limestone through inter-grinding were used to assess the mechanical behavior of PLC's. An additional commercially produced ASTM C150 Type I/III cement (OPC4) was used with ground limestone powders of varying fineness to create blended limestone cements (OPC4-CL and OPC 4-FL). The cement compositions can be seen in Table 3.2. The two ground limestone powders used had mean particle sizes of 1.3 μm (fine limestone, FL) and 10.8 μm (coarse limestone, CL).

The mean particle sizes, density, Blaine fineness, and percentage of calcium carbonate (CaCO_3) content by weight (if any) are summarized in Table 5.1. It should be noted that the CaCO_3 does not necessarily represent the actual percentage of limestone in the PLC's, as it is

TABLE 5.1
Mean particle size, density, Blaine fineness, and calcite content for each material

Material	Mean size	Density	Blaine fineness	CaCO_3
	μm	g/cm^3	m^2/kg	wt %
OPC 1	9.4	3.12	384	2.9
PLC 1	7.9	3.12	452	7.5
OPC 2	7.9	3.16	376	2.0
PLC 2	7.7	3.11	430	8.4
OPC 3	7.1	3.17	392	1.9
PLC 3	5.7	3.13	518	10.6
OPC 4	9.9	3.17	377	0.5
CL	10.8	2.70	321	97.2
FL	1.3	2.70	1069	99.5
FA	9.8	2.74	331	—

permissible to contain up to 25% (by mass) of impurities (15,16). For example, an 8% content of 75% pure CaCO_3 corresponds to approximately 11% total limestone content.

The coarse aggregate consisted of a #8 INDOT (47) graded limestone with a specific gravity of 2.75 and an absorption of 0.8% by mass. All coarse aggregate used in this study was sieved then recombined with the gradation shown in Table 5.2 to ensure that each mixture had comparable coarse aggregate volumes. The fine aggregate used was a normal weight natural river sand with a specific gravity of 2.58 and an absorption of 1.7% by mass. Tempered tap water at 23 ± 2 °C was used as the mixing water and a high range water reducing agent (HRWRA) was added at a rate of 0.1 g/g of cement.

5.2.2 Mixture Proportions

This study assessed eleven different cement systems at three water-to-powder ratios (w/p) for a total of thirty-three different concrete mixtures. The naming convention and binder proportions of each mixture can be seen in Table 5.3, with the aggregate proportions shown in Table 5.4. As mentioned, a total of four ordinary portland cements (OPCs), three complimentary portland limestone cements (PLCs), and two blended limestone cements were used to assess the effects of ground limestone additions in cementitious systems. Each of the blended limestone cements (OPC 4-FL and OPC 4-CL) had 15% of the cement replaced (by volume) with ground limestone. In order to assess

TABLE 5.2
Coarse aggregate gradation

Sieve Size	Percentage Passing
1	100%
3/4	91%
1/2	37%
3/8	16%
#4	2%
#8	0%

TABLE 5.3
Mixture proportions and naming conventions

Mixture	Water/ Powder (w/p)	Water/ Cement (w/c)	Ordinary Portland Cement (lbs/yd ³)	Portland Limestone Cement (lbs/yd ³)	Ground Limestone (by Volume) (%)	Fly Ash (by Volume)(%)	HRWRA (fl oz/ cwt)
0.38-OPC 1	0.38	0.38	604	—	—	—	11.4
0.42-OPC 1	0.42	0.42	571	—	—	—	5.7
0.46-OPC 1	0.46	0.46	542	—	—	—	1.4
0.38-PLC 1	0.38	0.41	—	598	—	—	11.4
0.42-PLC 1	0.42	0.45	—	566	—	—	5.7
0.46-PLC 1	0.46	0.49	—	537	—	—	2.8
0.38-OPC 2	0.38	0.39	604	—	—	—	11.4
0.42-OPC 2	0.42	0.43	571	—	—	—	5.7
0.46-OPC 2	0.46	0.47	542	—	—	—	1.4
0.38-OPC 2-FA	0.38	0.47	494	—	—	20	7.1
0.42-OPC 2-FA	0.42	0.52	467	—	—	20	2.8
0.46-OPC 2-FA	0.46	0.57	443	—	—	20	0.7
0.38-PLC 2	0.38	0.41	—	598	—	—	11.4
0.42-PLC 2	0.42	0.46	—	566	—	—	5.7
0.46-PLC 2	0.46	0.50	—	537	—	—	1.4
0.38-PLC 2-FA	0.38	0.50	—	486	—	20	8.5
0.42-PLC 2-FA	0.42	0.56	—	460	—	20	5.7
0.46-PLC 2-FA	0.46	0.61	—	437	—	20	2.8
0.38-OPC 3	0.38	0.38	604	—	—	—	11.4
0.42-OPC 3	0.42	0.42	571	—	—	—	5.7
0.46-OPC 3	0.46	0.46	542	—	—	—	1.4
0.38-PLC 3	0.38	0.41	—	598	—	—	11.4
0.42-PLC 3	0.42	0.45	—	566	—	—	5.7
0.46-PLC 3	0.46	0.49	—	537	—	—	1.4
0.38-OPC 4	0.38	0.38	604	—	—	—	11.4
0.42-OPC 4	0.42	0.42	571	—	—	—	5.7
0.46-OPC 4	0.46	0.46	542	—	—	—	1.4
0.38-OPC 4-CL	0.38	0.44	521	—	15	—	11.4
0.42-OPC 4-CL	0.42	0.48	493	—	15	—	5.7
0.46-OPC 4-CL	0.46	0.53	468	—	15	—	2.8
0.38-OPC 4-FL	0.38	0.44	521	—	15	—	11.4
0.42-OPC 4-FL	0.42	0.48	493	—	15	—	5.7
0.46-OPC 3-FL	0.46	0.53	468	—	15	—	2.8

the effects of fly ash on PLC's, two additional cement systems were created by replacing 20% of the cement (by volume) in OPC 2 and PLC 2 with a class C fly ash (FA). All eleven of these cement systems were evaluated at water-to-powder ratios (w/p) of 0.38, 0.42, and 0.46, corresponding to water-to-cement ratios (w/c) of approximately 0.41, 0.45, and 0.49 for PLC's and blended limestone cements. The concrete mixtures had an aggregate volume fraction of 75%, with a coarse to fine ratio of 55:45. The naming convention of follows the format of [w/p – (OPC/PLC) # – (FA/CL/FL)], where FA signifies a fly ash replacement, CL denotes a blended limestone-cement system with coarsely ground limestone (mean particle size of 17 μm), and FL denotes

TABLE 5.4
Saturated surface dry aggregate proportions

Volume fraction of Aggregate, %	75
Fine aggregate, lbs/yd ³	1478
Coarse aggregate, lbs/yd ³	1900

a blended limestone-cement system with finely ground limestone (mean particle size of 0.7 μm).

In certain test applications, concrete specimens were not suitable due to the relative size of the coarse aggregate. In these cases, equivalent mortar fractions were made using the same mixture designs as previously described, however the coarse aggregate was omitted and the batching water was adjusted to only account for the absorption of the fine aggregate.

5.2.3 Mixing Procedure

The mixing procedure was carried out in accordance with ASTM C192 (48). The concrete was made in 2.0 ft³ batches using a dual action, 3.0 ft³ capacity pan mixer. The materials were batched at a temperature of 23 ± 2 °C, with the aggregates being prepared in the oven dry state. The fine and coarse aggregate were combined in a “buttered” mixer first, adding a portion of the batch water to control dust and ensure proper water absorption for the aggregate. Next, the cement and

any additional supplementary materials (ground limestone and/or fly ash) were added to the mixer and combined with the aggregates until a uniform distribution was achieved. The remaining batch water was then added and the time of water to cement contact was noted. Immediately following the addition of water, the HRWRA was slowly added directly to the concrete mixture. The concrete was mixed for three minutes, rested for three minutes, and then mixed for an additional two minutes.

5.2.4 Time of Set

The time of set (TOS) was determined for equivalent mortar systems at a w/p of 0.42 using the penetration resistance method as described in ASTM C403 (49). A set of 6 in diameter by 6 in tall cylindrical samples were cast to study the initial and final setting. The samples were cast in two lifts, being vibrated and rodded 25 times after each lift. The samples were then capped and placed in an environmental chamber at a constant temperature of 23 ± 1 °C.

5.2.5 Compressive Strength

The compressive strength was determined in accordance with ASTM C39 (50). A set of 4 in diameter x 8 in tall (100 mm x 200 mm) cylinders were cast to study the compressive strength up to one year of age, with testing ages of 1, 3, 7, 14, 28, 90, 180, and 365 days. The cylinders were cast in two lifts, being vibrated and rodded 25 times after each lift. After one day of curing, the cylinders were demolded, sealed, and stored in a 100% relative humidity (RH) chamber at a temperature of 23 ± 1 °C until tested. For each day of testing, three cylinders were tested to determine the compressive strength of the mixtures. The cylinders were loaded at a rate of 35 ± 2 psi/s in a 700 kip hydraulic compression machine, utilizing neoprene end caps when tested.

5.2.6 Young's Modulus of Elasticity

The static modulus of elasticity (Young's modulus of elasticity) was determined using a procedure similar to that in ASTM C469 (51). A set of 4 in diameter x 8 in tall (100 mm x 200 mm) cylinders were cast to study the modulus of elasticity up to one year of age, with testing ages of 1, 3, 7, 14, 28, 90, 180, and 365 days. The cylinders were cast in two lifts, being vibrated and rodded 25 times after each lift. After one day of curing in their molds, the cylinders were demolded, sealed, and stored in a 100% RH chamber at a temperature of 23 ± 1 °C until tested. Upon testing, the cylinders were fitted with a compressometer equipped with a linear variable differential transformer (LVDT) displacement transducer. The cylinders were then loaded to 40% of their ultimate strength two separate times. The resulting slope of the stress-strain curve from the second loading was taken as the static modulus of elasticity. For each day of testing, two cylinders were tested for every

mixture with no cylinder being tested at more than one age.

5.2.7 Flexural Strength

The flexural strength of the mixtures was determined in accordance with ASTM C78 (52). For each mixture, two 6 in tall x 6 in deep x 21 in long beams were cast to study the flexural strength at an age of 7 days. The beams were cast in two lifts, being vibrated and rodded after each lift. After one day of curing in the molds, the beams were demolded, sealed in plastic, and stored in a 100% RH chamber at a temperature of 23 ± 1 °C. At six days of age the beams were unsealed and placed in a saturated lime water curing tank for 24 hours, at which point they were removed and wrapped in wet burlap until tested. The flexural strength of each mixture was determined under third-point loading, being loaded at a rate of 35 ± 5 lb/s.

5.2.8 Drying Shrinkage

The drying shrinkage was determined for two equivalent mortar mixtures in accordance with ASTM C157 (53). A series of 1 in tall x 1 in deep x 11.25 in long, prismatic specimens were cast to study the length change over time for both sealed and drying conditions at $50 \pm 1\%$ RH and 23 ± 1 °C. Each sample was cast in two lifts, being rodded and vibrated after each lift. After one day of curing in the molds, the samples were demolded and sealed with two layers of aluminum foil tape over the entire sample for the sealed specimens and over just the ends for the drying specimens. The length change over time was measured using a digital comparator with a precision of ± 0.0001 in.

5.2.9 Restrained Shrinkage

The dual ring test was used to quantify the autogenous deformations of two equivalent mortar mixtures. The dual ring testing device consists of two instrumented concentric invar restraining rings that operate in an insulated chamber (54,55). In this test, a mortar specimen was cast between the inner and outer rings in two lifts, being vibrated with a handheld vibrator after each lift then trowel finished upon completion. After casting, a copper tube and plate that is connected to a circulating water bath was loosely placed on top of the rings to maintain a constant temperature. Strain measurements were automatically recorded and used to determine the stress that builds up in the sample.

5.3 Results and Discussion

5.3.1 Time of Set

The initial and final times of set for each mixture evaluated at a w/p of 0.42 can be seen in Table 5.5. Inspection of the PLC systems relative to the OPC

TABLE 5.5
Setting time for mixtures evaluated at w/p of 0.42

Mixture	Time of Set (Hrs)	
	Initial	Final
0.42-OPC 1	4.5	5.8
0.42-PLC 1	3.7	4.8
0.42-OPC 2	4.3	5.8
0.42-OPC 2-FA	4.8	6.2
0.42-PLC 2	4.3	5.5
0.42-PLC 2-FA	4.3	5.6
0.42-OPC 3	4.3	5.6
0.42-PLC 3	4.0	5.2
0.42-OPC 4	6.2	7.8
0.42-OPC 4-CL	6.3	7.4
0.42-OPC 4-FL	4.2	5.8

counterparts shows an average reduction of 10% in initial and final set is observed. The same reduction of 10% in set times was also observed when FA was used with the PLC. When limestone powders are blended with the cement, the initial and final set times are dependent on the particle size of the limestone used. In the case of the FL, the set time was accelerated by two hours while the CL shortened the final set time by 5%. In these blended systems, the setting time can be selectively modified through increasing (i.e., larger particles than the cement) or decreasing (smaller particles than the cement) the space that needs to be bridged by hydration products. These findings are consistent with previous research where Bentz et al. demonstrated that through varying the fineness of limestone additions the set time of high volume fly ash systems could be regulated (8,56).

5.3.2 Compressive Strength

The compressive strength of each mixture up to an age of one year can be seen in Figures 5.1, 5.2, 5.3, 5.4,

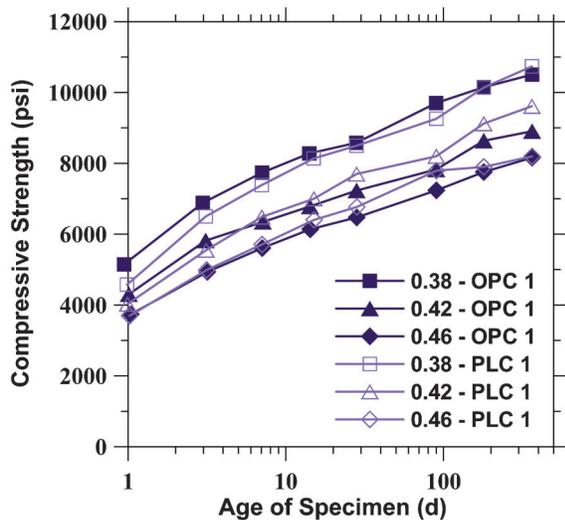


Figure 5.1 Compressive strength up to one year of age for OPC 1 and PLC 1 at w/p of 0.38, 0.42, and 0.46.

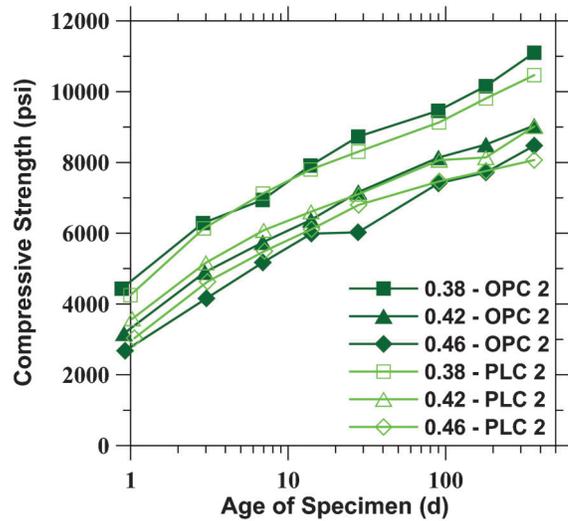


Figure 5.2 Compressive strength up to one year of age for OPC 2 and PLC 2 at w/p of 0.38, 0.42, and 0.46.

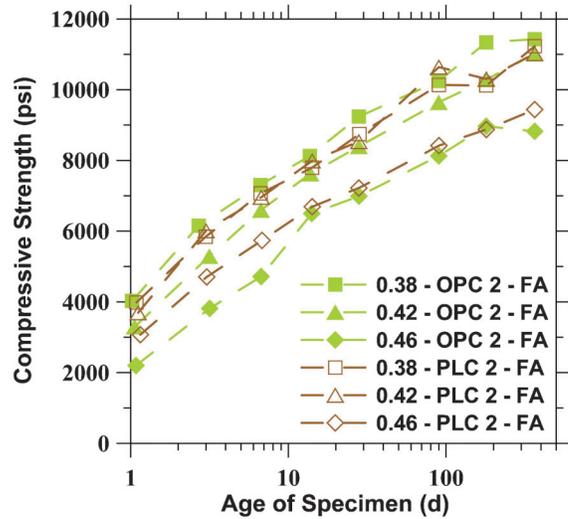


Figure 5.3 Compressive strength up to one year of age for OPC 2-FA and PLC 2-FA at w/p of 0.38, 0.42, and 0.46.

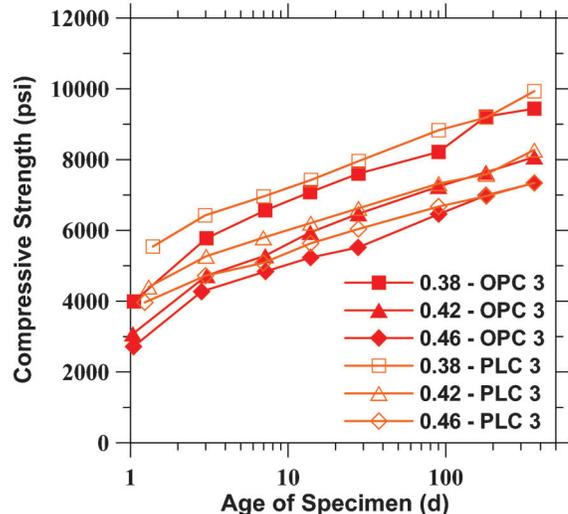


Figure 5.4 Compressive strength up to one year of age for OPC 3 and PLC 3 at w/p of 0.38, 0.42, and 0.46.

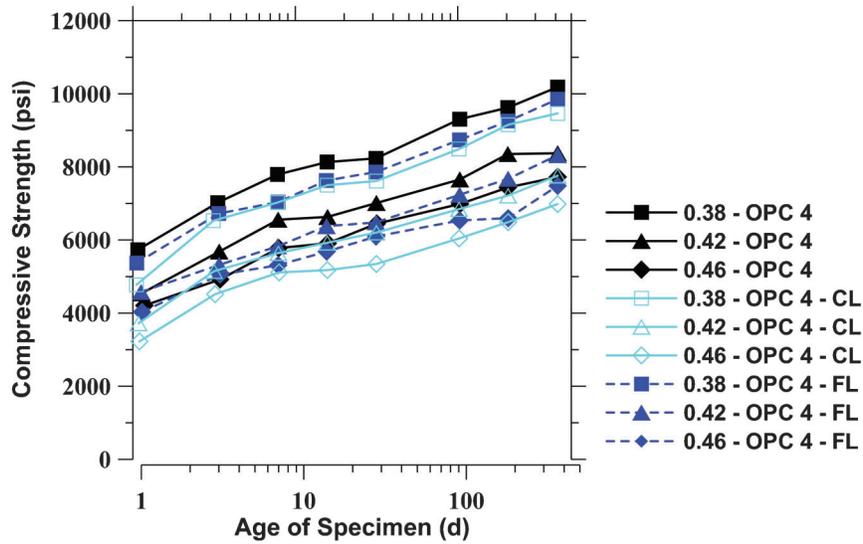


Figure 5.5 Compressive strength up to one year of age for OPC 4, OPC 4-CL, and OPC 4-FL at w/p of 0.38, 0.42, and 0.46.

and 5.5. Figure 5.6 shows the normalized compressive strength of all limestone systems relative to their OPC counterparts (PLC/OPC). The discussion that follows will address each comparison being assessed individually.

1. The first trend that can be noticed is the relative performance of the PLC systems. In general, an initial increase in relative compressive strength is seen in the PLCs at early ages but this improvement diminishes with age. At 28 days of age, the PLC 1, PLC 2, and PLC 3 cements exhibited an average increase in strength of 1.5%, with a maximum reduction of 6% at any w/p.

2. A comparison of the interground cements with the blended cements shows two distinctly different trends. As mentioned, the PLC systems exhibit higher early age strengths and achieve similar 28 day strengths in comparison to their reference. In contrast to this, the blended limestone cements (OPC 4-FL, OPC 4-CL) exhibit an average reduction at any given age or w/p of 8.5% with a maximum strength loss of 20%.

3. In general, the influence of w/p on the relative compressive strength of the PLCs (i.e., the comparison of OPC to PLC) is negligible, as seen in Figure 5.6. Likewise, the OPC 4-FL systems show a consistent

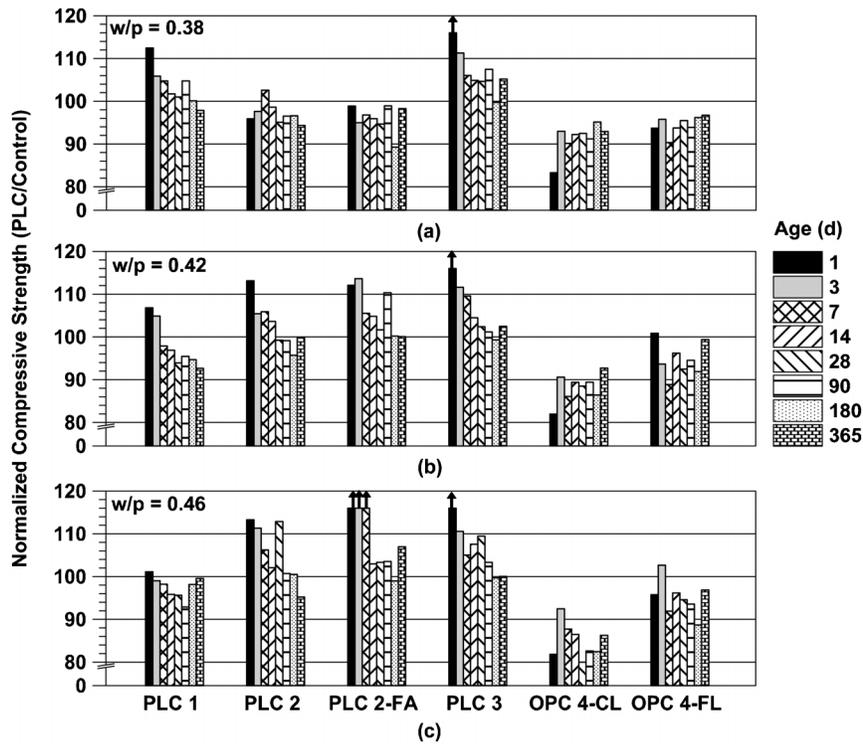


Figure 5.6 Normalized compressive strength of limestone cement systems with w/p of (a) 0.38, (b) 0.42, and (c) 0.46.

average reduction in strength of 5% across all w/p. The OPC 4-CL systems, however, show an increasing reduction in strength with increasing w/p. This trend is likely due to the increasing amounts excess water due to the filler effect which yields a larger quantity of capillary pores, in turn reducing strengths.

4. When the effects of limestone fineness in the blended cements is analyzed, the general trend seen is that finer limestone additions result in a smaller reduction in strength (from 5% for OPC 4-FL to 12% for OPC 4-CL). As previously discussed, this is mostly a consequence of the difference in particle packing of each of these systems. The presence of the CL in the cement systems cause larger initial particle spacing (57,58) which must be bridged by hydration products. The result is a slower rate of hydration as discussed in chapter 3 which leads to a reduction in strength gain.
5. When the influence of fly ash in these systems is assessed, two observations can be made. The first is evident from a comparison of Figure 5.3 with Figure 5.2, showing that the inclusion of fly ash in either OPCs or PLCs leads to higher absolute strengths after 7 days. The second observation can be made from Figure 5.6, where the PLC 2-FA system shows a relative increase in strength of more than 10% at early ages for w/p of 0.42 and 0.46. This suggests that the increased rate of hydration of the PLC is able to overcome the slow early age reactions typically seen in mixtures containing FA. The result is a mixture that has the benefit of improved long-term performance due to the presence of FA without the slow onset of strength gain.

5.3.3 Young's Modulus of Elasticity

The modulus of elasticity for each mixture up to an age of one year can be seen in Figure 5.7, 5.8, 5.9, 5.10, and 5.11. Figure 5.12 shows the normalized modulus of elasticity of all limestone systems relative to their OPC counterparts (PLC/OPC). The discussion of the results

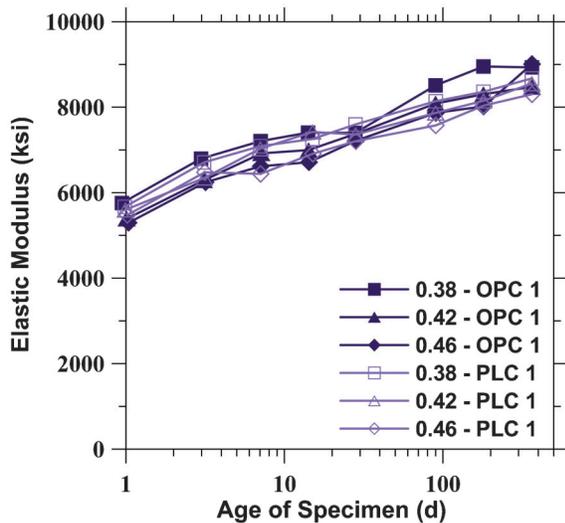


Figure 5.7 Modulus of elasticity up to one year of age for OPC 1 and PLC 1 at w/p of 0.38, 0.42, and 0.46.

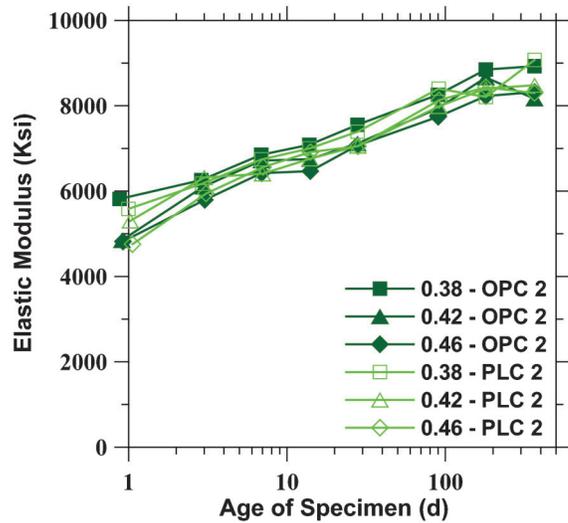


Figure 5.8 Modulus of elasticity up to one year of age for OPC 2 and PLC 2 at w/p of 0.38, 0.42, and 0.46.

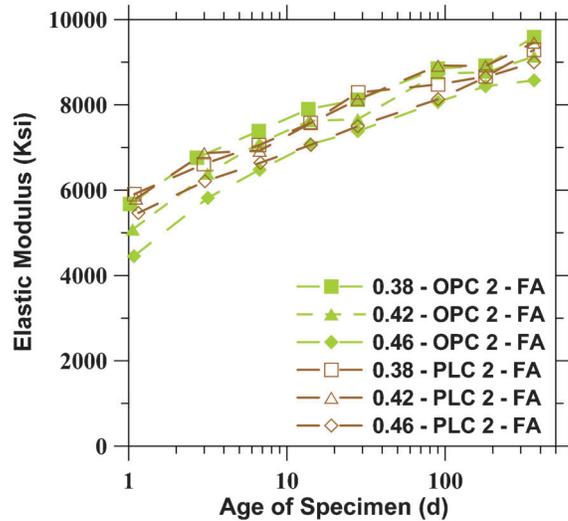


Figure 5.9 Modulus of elasticity up to one year of age for OPC 2-FA and PLC 2-FA at w/p of 0.38, 0.42, and 0.46.

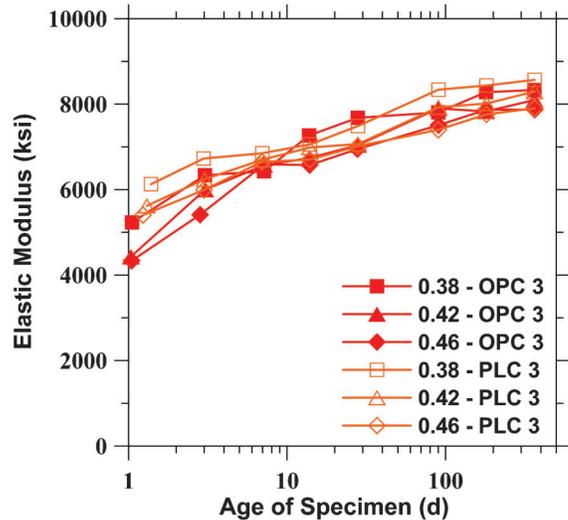


Figure 5.10 Modulus of elasticity up to one year of age for OPC 3 and PLC 3 at w/p of 0.38, 0.42, and 0.46.

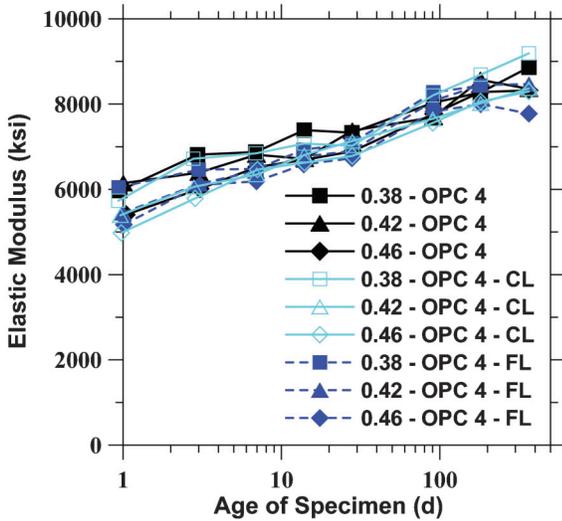


Figure 5.11 Modulus of elasticity up to one year of age for OPC 4, OPC 4-CL, and OPC 4-FL at w/p of 0.38, 0.42, and 0.46.

will again follow in line with the key comparisons outlined in the introduction.

1. Figure 5.12 shows that in general a negligible difference exists between the PLCs compared to their OPC reference. The maximum reduction in elastic modulus of any PLC at any age or w/p is 7%. This slight reduction can be attributed mostly to the replacement of hydration products with a ground limestone powder that is slightly

2. Comparing the effect of intergrinding with blending the limestone shows that the only noticeable difference is the onset of stiffness at early ages. The blended cements have reductions in modulus of elasticity greater than 5% in some cases, whereas the PLCs do not exhibit any significant early age reductions with some cases actually demonstrating an increase in stiffness. This is not surprising as the hydration of the interground cements is generally faster than that of the blended cements.
3. Comparing Figure 5.12(a), (b), and (c) shows that the reduction in stiffness is more pronounced at lower w/p. At higher w/p, the behavior of the system is highly dependent on the capillary pore structure resulting in similar performance between the PLCs and OPCs. At lower w/p, the effects of diluting a portion of hydration products with the less dense limestone particles is more apparent as the capillary porosity has been minimized, altering the behavior of the material.
4. A comparison of the different particle sizes of limestone used in the blended limestone cements show little to no effect on the modulus of elasticity.
5. Figure 5.9 shows that the replacement of cement with fly ash results in higher absolute values of modulus of elasticity compared to systems with no fly ash. This increase in elastic modulus occurs regardless of limestone content, while as Figure 5.12 shows, when fly ash is used with a PLC, an additional increase can be seen at early ages. The increase in stiffness in either the OPC or PLC cements can be attributed to the further densification of the microstructure due to the conversion of calcium hydroxide (CH) to calcium-silicate-hydrate (CSH) as the FA reacts.

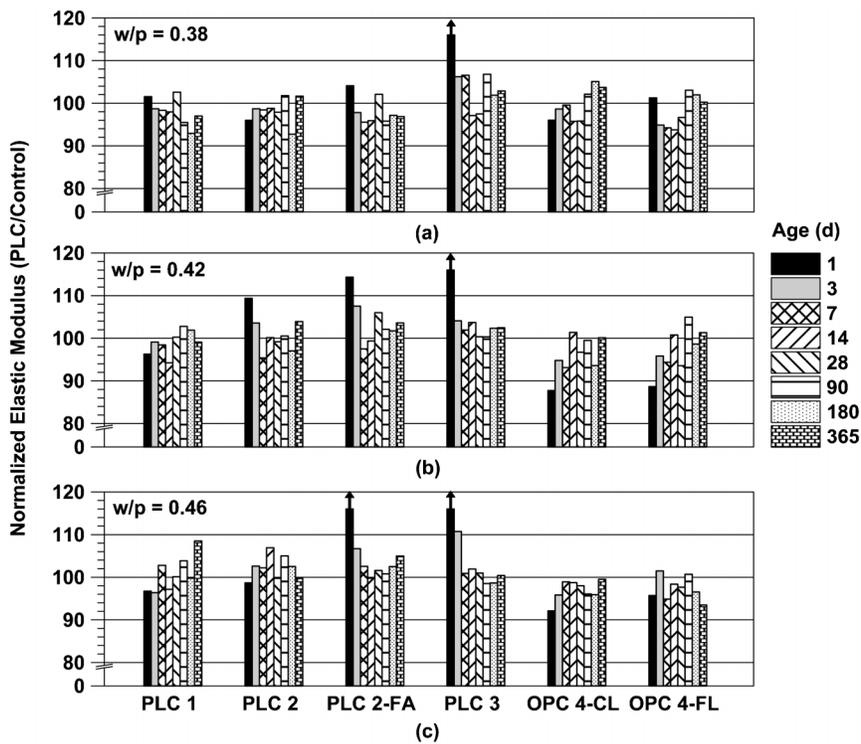


Figure 5.12 Normalized modulus of elasticity of portland limestone cements with w/p of (a) 0.38, (b) 0.42, and (c) 0.46.

5.3.4 Flexural Strength

Figure 5.13 shows the normalized flexural strength (PLC/Control) for each limestone cement system at an age of 7 days. The flexural strength for each mixture has been provided in Table 5.6. A comparison of PLC 1, 2, and 3 concretes relative to their control mixture (OPC) shows an average increase of 3% across all w/p, with a maximum reduction of 6%. The most significant change in flexural strength can be seen when comparing the PLC cements to the blended limestone cements. The trend present in the PLCs suggests similar flexural strengths can be achieved whereas the blended cements show an average reduction of 9%. It should also be noted that this reduction in flexural strength increases with decreasing limestone particle size, from 6% for the CL to 12% for the FL. In general, the reduction in flexural strength increases with increasing w/p for the blended limestone cements but remains mostly constant for the PLCs across all w/p. When fly ash is included in the system, an average increase in flexural strength of 7% is observed. Table 5.6 shows that the flexural strength of the OPC 2-FA system is similar to OPC 2 and while an increase of 5% is observed in the PLC 2-FA system in comparison to PLC 2. It should be noted here, however, that all of the mixtures tested were well above the 550 psi limit set forth by INDOT specifications.

5.3.5 Volume Change

The results of the free shrinkage of sealed and unsealed shrinkage prisms at 50% RH for 0.38-OPC 2 and 0.38-PLC 2 can be seen in Figure 5.14. As can be seen, the OPC and PLC mortars exhibit similar shrinkage under sealed conditions whereas the PLC mortar shows 5% more shrinkage strain at 28 days when exposed to drying (unsealed). This is consistent with recent research which showed that interground PLC mortars have similar capillary porosity but more gel porosity in comparison to an OPC reference mortar

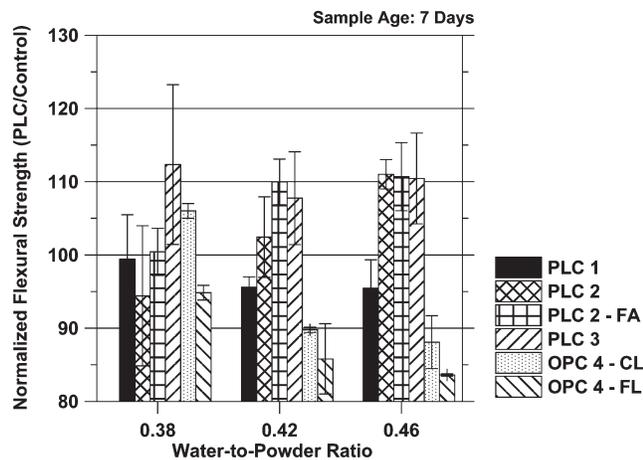


Figure 5.13 Normalized flexural strength at 7 days of age for limestone cement systems at w/p of 0.38, 0.42, and 0.46.

TABLE 5.6 Flexural strength (\pm one standard deviation) for each mixture at 7 days of age

Mixture	Flexural Strength at 7 Days (psi)
0.38-OPC 1	1010 \pm 10
0.42-OPC 1	950 \pm 15
0.46-OPC 1	840 \pm 30
0.38-PLC 1	1000 \pm 60
0.42-PLC 1	910 \pm 5
0.46-PLC 1	800 \pm 20
0.38-OPC 2	1070 \pm 100
0.42-OPC 2	870 \pm 45
0.46-OPC 2	810 \pm 10
0.38-OPC 2-FA	1050 \pm 15
0.42-OPC 2-FA	920 \pm 10
0.46-OPC 2-FA	790 \pm 30
0.38-PLC 2	1010 \pm 40
0.42-PLC 2	890 \pm 15
0.46-PLC 2	900 \pm 15
0.38-PLC 2-FA	1060 \pm 30
0.42-PLC 2-FA	1010 \pm 30
0.46-PLC 2-FA	880 \pm 10
0.38-OPC 3	860 \pm 55
0.42-OPC 3	780 \pm 35
0.46-OPC 3	710 \pm 10
0.38-PLC 3	970 \pm 70
0.42-PLC 3	840 \pm 35
0.46-PLC 3	780 \pm 40
0.38-OPC 4	1040 \pm 5
0.42-OPC 4	990 \pm 5
0.46-OPC 4	980 \pm 5
0.38-OPC 4-CL	1100 \pm 15
0.42-OPC 4-CL	890 \pm 5
0.46-OPC 4-CL	860 \pm 35
0.38-OPC 4-FL	980 \pm 5
0.42-OPC 4-FL	850 \pm 50
0.46-OPC 3-FL	820 \pm 5

(59). It has been demonstrated that relative humidities below 80% result in the drying of these gel pores, which is consistent with the slight increase in drying shrinkage shown below.

Figure 5.15 shows the stress that develops in the dual ring test when the material shrinkage is restrained from shrinking. It can be seen that the 0.38-OPC 2 and 0.38-PLC 2 mortar systems exhibit the similar shrinkage behavior over the first 72 hours, at which point the 0.38-PLC 2 mortar shows less stress development. At an age of approximately 168 hours, the temperature of the samples was decreased at 2 °C/h until the specimen cracked (seen on Figure 5.15 as a vertical line). The resulting increase in stress until cracking is a measure of the remaining capacity of the sample, equal to 2.1 MPa for 0.38-PLC 2 and 2.0 MPa for 0.38-OPC 2, showing that there is not a significant increase in risk for shrinkage cracking in interground limestone cements, consistent with Barrett, et al. (59).

It should however be noted that previous work has shown that the shrinkage cracking potential in blended mixtures depends on the size of the blended powders (5).

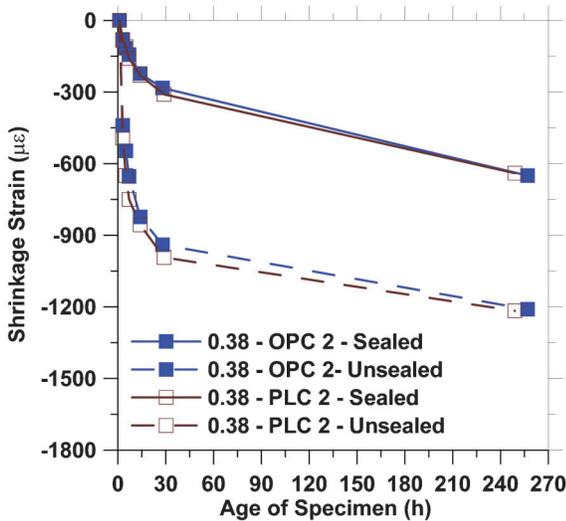


Figure 5.14 Free shrinkage of sealed and unsealed equivalent mortar prisms for 0.38-OPC 2 and 0.38-PLC 2.

5.4 Summary and Conclusions

This chapter investigated the mechanical behavior of systems containing ground limestone. The results of this chapter can be summarized as:

- The time of set for the PLCs was on average 10% earlier than OPCs, while the time of set of blended limestone systems is dependent on the particle size of limestone used. The fine limestone accelerates set while the coarse limestone retarded set.
- Generally, PLCs show an increase in compressive strength at early ages that diminishes with time, resulting in similar compressive strengths at 28 days of age. This is consistent with the finer grind that leads to higher early strength. The blended limestone cements had an average reduction in strength of 8.5% with this deficit increasing at higher w/p. This is consistent with the effects of dilution.
- Slight reductions in Young's modulus of elasticity were observed due to the dilution of hydration products with

relatively softer limestone particles. This trend was more evident at lower w/p. In some instances, the onset of stiffness of the blended limestone systems was inhibited, with reductions in elastic modulus as much as 12%.

- The flexural strength of the PLCs at 7 days of age was similar to the OPCs at all w/p tested. In contrast to this, the blended limestone cements showed increasing reductions in flexural strength with both increasing w/p and limestone particle size.
- No significant change in drying shrinkage or restrained shrinkage cracking was observed for the PLC 2 cement. Although no tests were performed here, it should be noted that previous studies have shown that systems with fine inclusions (such as the blended limestone cements) have shown increased susceptibility to shrinkage and cracking.

6. EVALUATION OF THE TRANSPORT PROPERTIES IN SYSTEMS CONTAINING LIMESTONE ADDITIONS

6.1 Introduction

The intent of introducing portland limestone cements (PLCs) under ASTM C595 is to address the growing concerns of sustainability in cement and concrete production by providing a replacement for ASTM C150 Type I/II ordinary portland cements (OPCs) that achieves similar performance while reducing clinker content. This chapter presents results on the transport properties of these PLCs as assessed through standardized testing methods, while evaluating the following five variables:

1. OPC versus PLC
2. Interground limestone cements (PLCs) versus blended limestone cements
3. Varying water-to-powder ratios (w/p) of 0.38, 0.42, and 0.46 (representing the upper, middle, and lower bounds as permissible under INDOT specifications)
4. Effect of particle size of ground limestone used in blended limestone cement systems

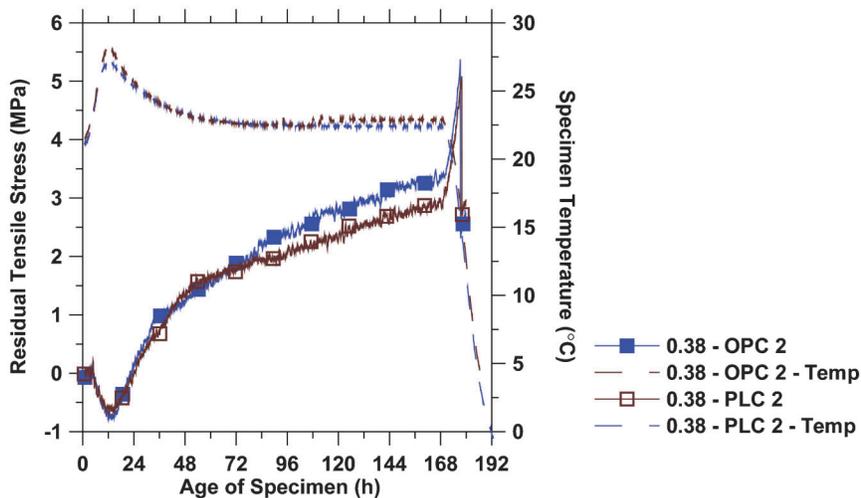


Figure 5.15 Tensile stress development in the dual ring test for 0.38-OPC 2 and 0.38-PLC 2.

5. Effect of including fly ash in OPC versus PLC cement systems

The transport properties tested include the chloride diffusion coefficients and tortuosity as determined through Stadium Lab, the bulk resistivity, and water absorption.

6.2 Materials and Methods

6.2.1 Materials

Three commercially produced, ASTM C150 Type I/II (I) ordinary portland cements (OPC 1-3) with complimentary ASTM C595 Type IL (I6) portland limestone cements (PLC 1-3) containing 10% to 15% replacement of cement by limestone through inter-grinding were used to assess the mechanical behavior of PLC's. An additional commercially produced ASTM C150 Type I/III cement (OPC4) was used with ground limestone powders of varying fineness to create blended limestone cements (OPC4-CL and OPC 4-FL). The cement compositions can be seen in Table 3.2. The two ground limestone powders used had mean particle sizes of 1.3 μm (fine limestone, FL) and 10.8 μm (coarse limestone, CL).

The mean particle sizes, density, Blaine fineness, and percentage of calcium carbonate (CaCO_3) content by weight (if any) are summarized in Table 5.1. It should be noted that the CaCO_3 does not necessarily represent the actual percentage of limestone in the PLC's, as it is permissible to contain up to 25% (by mass) of impurities (15,16). For example, an 8% content of 75% pure CaCO_3 corresponds to approximately 11% total limestone content.

The coarse aggregate consisted of a #8 INDOT (47) graded limestone with a specific gravity of 2.75 and an absorption of 0.8% by mass. All coarse aggregate used in this study was sieved then recombined with the gradation shown in Table 5.2 to ensure that each mixture had comparable coarse aggregate volumes. The fine aggregate used was a normal weight natural river sand with a specific gravity of 2.58 and an absorption of 1.7% by mass. Tempered tap water at $23 \pm 2^\circ\text{C}$ was used as the mixing water and a high range water reducing agent (HRWRA) was added at a rate of 0.1 g/g of cement.

6.2.2 Mixture Proportions

This study assessed eleven different cement systems at three water-to-powder ratios (w/p) for a total of thirty-three different concrete mixtures. The naming convention and binder proportions of each mixture can be seen in Table 5.3, with the aggregate proportions shown in Table 5.4. As mentioned, a total of four ordinary portland cements (OPCs), three complimentary portland limestone cements (PLCs), and two blended limestone cements were used to assess the effects of ground limestone additions in cementitious

systems. Each of the blended limestone cements (OPC 4-FL and OPC 4-CL) had 15% of the cement replaced (by volume) with ground limestone. In order to assess the effects of fly ash on PLC's, two additional cement systems were created by replacing 20% of the cement (by volume) in OPC 2 and PLC 2 with a class C fly ash (FA). All eleven of these cement systems were evaluated at water-to-powder ratios (w/p) of 0.38, 0.42, and 0.46, corresponding to water-to-cement ratios (w/c) of approximately 0.41, 0.45, and 0.49 for PLC's and blended limestone cements. The concrete mixtures had an aggregate volume fraction of 75%, with a coarse to fine ratio of 55:45. The naming convention follows the format of [w/p - (OPC/PLC) # - (FA/CL/FL)], where FA signifies a fly ash replacement, CL denotes a blended limestone-cement system with coarsely ground limestone (mean particle size of 17 μm), and FL denotes a blended limestone-cement system with finely ground limestone (mean particle size of 0.7 μm).

6.2.3 Mixing Procedure

The mixing procedure was carried out in accordance with ASTM C192 (48). The concrete was made in 2.0 ft^3 batches using a dual action, 3.0 ft^3 capacity pan mixer. The materials were batched at a temperature of $23 \pm 2^\circ\text{C}$, with the aggregates being prepared in the oven dry state. The fine and coarse aggregate were combined in a "buttered" mixer first, adding a portion of the batch water to control dust and ensure proper water absorption for the aggregate. Next, the cement and any additional supplementary materials (ground limestone and/or fly ash) were added to the mixer and combined with the aggregates until a uniform distribution was achieved. The remaining batch water was then added and the time of water to cement contact was noted. Immediately following the addition of water, the HRWRA was slowly added directly to the concrete mixture. The concrete was mixed for three minutes, rested for three minutes, and then mixed for an additional two minutes.

6.2.4 Migration Cell and Stadium Lab

The diffusion coefficients for ionic species were measured using Stadium Lab and a migration cell. The test method is a modified version of ASTM C1202 (60), where the intensity of electrical current passed through a 4 in diameter by 2 in thick (100 mm x 50 mm) cylindrical specimen is monitored over a 14 day period. The samples used for this test were cut from a set of 4 in diameter by 8 in long concrete cylinders that were sealed and placed in a chamber at 100% RH and $23 \pm 2^\circ\text{C}$ for 90 days. After the samples were cut, the sides of the samples were sealed with an epoxy after which they were vacuum saturated with 0.3 M NaOH for approximately 18 hours. Once saturated, the samples were mounted between a cell filled with 0.3 M NaOH solution (downstream) and a cell filled with 0.5 M NaCl + 0.3 M NaOH solution (upstream). A constant

DC potential of 20 V was maintained across the specimen for 14 days while the voltage, current, and temperature were measured and recorded at 15 minute intervals.

In conjunction with the migration cell testing, the volume of permeable voids of the samples was determined in accordance with ASTM C642 (61) (with the exception that boiling was replaced with vacuum saturation). For this test, additional 4 in diameter by 2 in thick samples were cut from 4 in diameter by 8 in tall cylinders at an age of 90 days, sealed on the lateral sides, and placed in an environmental chamber at 50% RH and 23 °C. The mass change of the samples was monitored until a mass equilibrium of $\pm 0.5\%$ was reached, at which point the samples were oven dried then vacuum saturated. Using the oven dry mass, saturated mass, buoyant mass, and conditioned mass, the volume of permeable voids was able to be determined. The results from the migration cell and the volume of permeable voids were entered into STADIUM Lab software to evaluate the ion diffusion coefficients and the tortuosity of the samples (62).

6.2.5 Bulk Resistivity

The bulk resistivity of the concrete mixtures was measured in accordance with the testing protocol as recommended by Spragg, et al. (63). A set of 4 in diameter x 8 in tall (100 mm x 200 mm) cylinders were cast to study the bulk resistivity up to one year of age, with testing ages of 1, 3, 7, 14, 28, 90, 180, and 365 days. The cylinders were cast in two lifts, being vibrated and rodded 25 times after each lift. After one day of curing in their molds, the cylinders were demolded, sealed in plastic bags, and stored in a 100% RH chamber at a temperature of 23 ± 1 °C until tested to minimize evaporation. At each age of testing, the cylinders were connected to a resistance meter via metal caps placed on both ends of the cylinder with wet sponges between the cap and cylinder to ensure proper contact. The bulk resistivity was calculated by multiplying the resistance by the geometry factor (k) equal to the area of the cylinder divided by the length of the cylinder. It should be noted that the same samples were tested over the varying ages, being re-sealed in bags and placed back in a 100% RH chamber until the next testing age.

It should be noted that the samples were stored in a sealed condition, the samples cannot be considered to be saturated. This is an important consideration, as previous research has shown that changes in degree of saturation (DOS) change the measured bulk resistivity (64). In contrast to this, recent research has also shown that storing samples in curing tanks in an effort to ensure a high DOS throughout the duration of testing leads to excessive leeching in the samples (65). For this work, it was determined that the consequence of leeching was decidedly destructive to the results while the differences in DOS between the OPC and PLC samples was found to be minimal.

6.2.6 Water Absorption and Degree of Hydration

The rate of water absorption for each concrete mixture was determined in accordance with a modified version of ASTM C1585 (66). A set of 4 in diameter x 8 in tall (100 mm x 200 mm) cylinders were cast in two lifts, being vibrated and rodded 25 times after each lift. After one day of curing in their molds, the cylinders were demolded, sealed in plastic bags, and stored in a 100% RH chamber at a temperature of 23 ± 1 °C until 28 days of age, at which point 4 in diameter by 2 in thick (100 mm x 50 mm) were cut from the middle 6 in section of these samples using a concrete wet saw. Once cut, the sides of the samples were sealed with epoxy then the samples were conditioned in an environmental chamber at $50 \pm 1\%$ RH and 23 ± 1 °C until they reached a mass equilibrium of $\pm 0.01\%$ (a time period of approximately 12 to 14 months). Prior to testing, the top of the samples were sealed with plastic and the initial mass was recorded. The samples were then placed on supports inside containers which were then filled with water such that the water level was approximately 1/8 in (3 mm) above the bottom of the sample. The mass of each sample was then taken at the prescribed intervals set forth in ASTM C1585 with the test ending after 8 days of absorption.

Upon completion of the absorption testing, the degree of saturation of each of these samples was determined by first oven drying the samples until a mass equilibrium of $\pm 0.01\%$ was reached, at which point the samples were then vacuum saturated. Using the initial conditioned mass, the oven dry mass, and the saturated mass, the degree of saturation was able to be calculated for each sample.

6.3 Results and Discussion

6.3.1 Migration Cell and Stadium Lab

The results from the migration cell testing can be seen in Table 6.1. These results include the volume of permeable voids as measured by ASTM C642 (61) and the chloride diffusion coefficient and tortuosity as calculated using Stadium Lab from the results of the migration cell testing. It should be noted here that, due to the method in which Stadium Lab reports its results, the chloride diffusion coefficient and tortuosity are directly proportional for any given mixture. Comparing PLCs with OPCs shows that the PLC's have slightly higher volumes of permeable voids, with an increase of up to 10% in voids. The calculated chloride diffusion coefficients for PLC 1 and 2 show an average increase of nearly 30% relative to their OPC counterparts, with the same increase in tortuosity in these systems. In contrast to this, PLC 3 demonstrated just a 2% increase in chloride diffusion coefficient and tortuosity. Comparing OPC 4-CL and OPC 4-FL with OPC 4 shows that the blended limestone systems have between 2% and 4% more permeable voids, while the chloride diffusion coefficients increased by 17% and 8% for the

TABLE 6.1

Volume of permeable voids, chloride diffusion coefficients, and tortuosity as determined through migration cell testing in conjunction with Stadium Lab

Mixture	Volume of Permeable Voids (%)	Cl ⁻ Diffusion Coefficient (10^{-11} m ² /s)	Tortuosity
0.42-OPC 1	10.4	4.40	0.0217
0.42-PLC 1	11.0	5.57	0.0274
0.42-OPC 2	11.4	4.97	0.0245
0.42-OPC 2-FA	9.8	1.82	0.0089
0.42-PLC 2	11.5	6.49	0.0320
0.42-PLC 2-FA	10.0	0.77	0.0038
0.42-OPC 3	10.6	6.35	0.0313
0.42-PLC 3	11.5	6.46	0.0318
0.42-OPC 4	10.7	6.22	0.0306
0.42-OPC 4-CL	10.1	7.26	0.0357
0.42-OPC 4-FL	11.1	6.73	0.0331

CL and FL respectively. Collectively, these results suggest that the chloride diffusion coefficient for cementitious materials containing limestone may increase anywhere from 2% to 30%, with the magnitude of this increase being related to the size of the limestone particles. Furthermore, the results from the Stadium Lab suggest that changes in tortuosity are mostly responsible for the changes in chloride diffusion coefficients.

When fly ash is included in either an OPC or PLC, the volume of permeable voids is reduced by an average of 13.5%. In addition to this, the tortuosity of the OPC 2-FA and PLC 2-FA mixtures (compared to their counterparts without fly ash) is reduced by 64% and 88%, respectively. These improvements in tortuosity result in the same improvements in chloride diffusion coefficients. It should also be noted that when fly ash was used with a PLC, a reduction in tortuosity of 58% is observed relative to the OPC system with fly ash.

6.3.2 Bulk Resistivity

The bulk resistivity was measured for each mixture up to an age of one year can be seen in Figure 6.1, 6.2, 6.3, 6.4, and Figure 6.5. Figure 6.6 shows the normalized bulk resistivity for each limestone cement system (PLC/Control). The bulk resistivity is an intrinsic measure of the microstructural development of the concrete, yielding information about the volume of pores in the system. Before discussing the results, it should first be noted that the bulk resistivity of concrete is a function of not only the pore volume, but also the connectivity of the pores and the pore solution resistivity, all of which change with time (63,67). For the results presented here, it is important to know that the samples were tested under sealed conditions (being sealed in plastic bags and stored in a 100% RH chamber to prevent drying) and were therefore are not in a saturated condition. The results in section 6.3.3 however suggest that no large differences in degree of saturation (DOS) between the PLCs and OPCs should be anticipated. It is anticipated that the pore solution

resistivity varies between each of the mixtures and may be affected by the presence of limestone (due to the formation of carboaluminates), however the testing of the pore solution resistivities for these mixtures was inconclusive and may need further investigation.

A comparison of the PLCs with the OPCs shows an average reduction in bulk resistivity at any age or w/p of approximately 25% for PLC 1 and 15% for PLC 2, as seen in Figure 6.6. In contrast to these two mixtures, PLC 3 showed an average increase in bulk resistivity of 18% at any age or w/p. These results suggest that the bulk resistivity of PLCs may be related to the particle size distribution and they are reasonably consistent with the migration cell testing, however in this case it is not known whether these changes in bulk resistivity are a result of the limestone modifying the pore solution resistivity, the tortuosity, or both. Further investigations will be needed to determine the extent to which each of these variables affect the bulk resistivity.

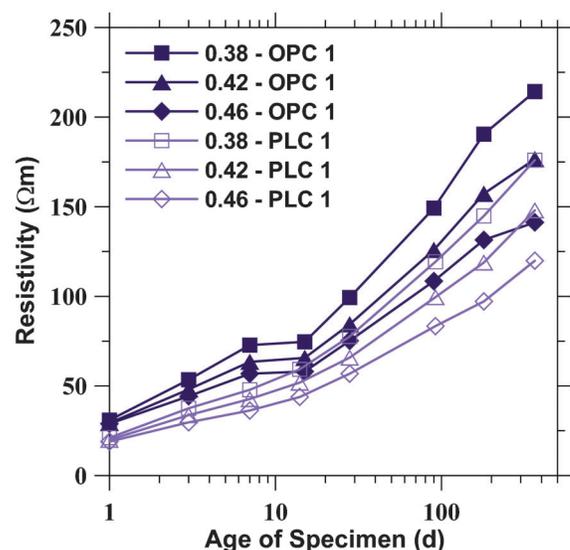


Figure 6.1 Bulk resistivity up to one year of age for OPC 1 and PLC 1 at w/p of 0.38, 0.42, and 0.46.

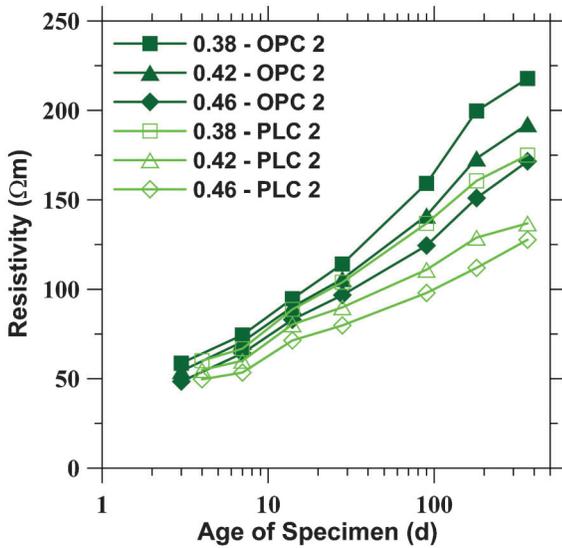


Figure 6.2 Bulk resistivity up to one year of age for OPC 2 and PLC 2 at w/p of 0.38, 0.42, and 0.46.

The bulk resistivity of the blended limestone systems (OPC 4-CL and OPC 4-FL) show a different trend than the PLCs, being dependent on the w/p and independent of limestone fineness. Figure 6.6 shows that both the CL and FL cementitious systems have approximately the same average bulk resistivity at any w/p, differing by $\pm 3\%$. At w/p of 0.38 and 0.42, these systems exhibit an average increase in bulk resistivity of up to 25% and 5% respectively, while at a w/p of 0.46 they show an average reduction of -20%.

The bulk resistivity of the cementitious systems containing fly ash showed increases of up to an order of magnitude in the bulk resistivity of the material, as seen by comparing Figure 6.2 with Figure 6.3. Figure 6.6b and c show that at a w/p of 0.42 and

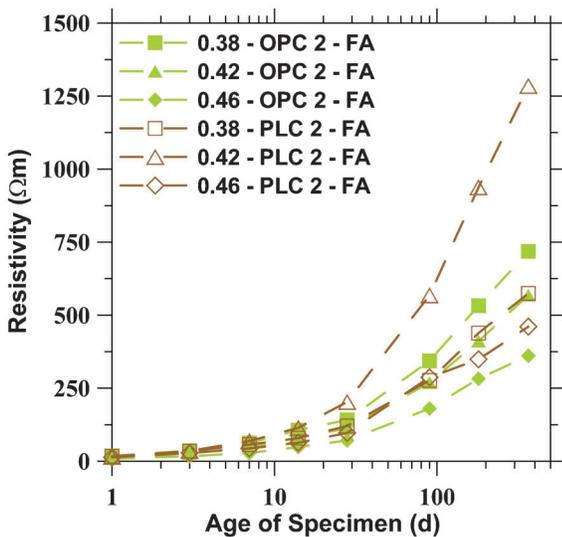


Figure 6.3 Bulk resistivity up to one year of age for OPC 2-FA and PLC 2-FA at w/p of 0.38, 0.42, and 0.46.

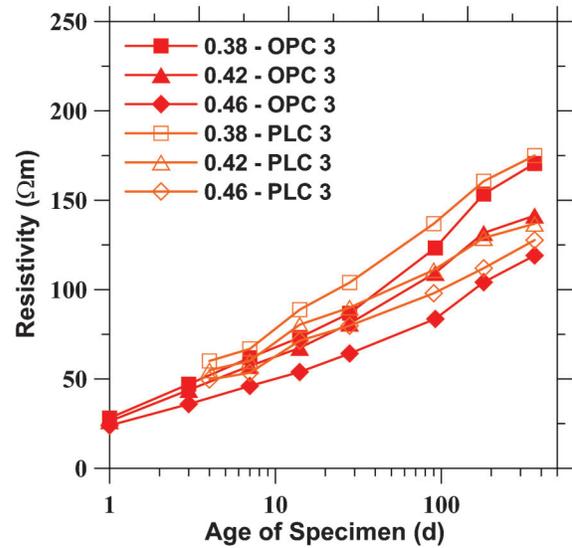


Figure 6.4 Bulk resistivity up to one year of age for OPC 3 and PLC 3 at w/p of 0.38, 0.42, and 0.46.

0.46 the presence of limestone (PLC 2-FA) acts to enhance the overall performance (80% and 35%, respectively) of the system relative to OPC 2-FA. This improvement due the presence of limestone may be related to particle packing (it was shown in section 4.3.1.3 that the DOH of 0.42-OPC 2-FA and 0.42-PLC 2-4 are similar) however more work should be done to determine these effects.

6.3.3 Water Absorption and Degree of Saturation

The results of the ASTM C1585 (64) water absorption test and the associated change in degree of saturation (DOS) for each mixture can be seen in Figure 6.7 through Figure 6.17. The initial and secondary

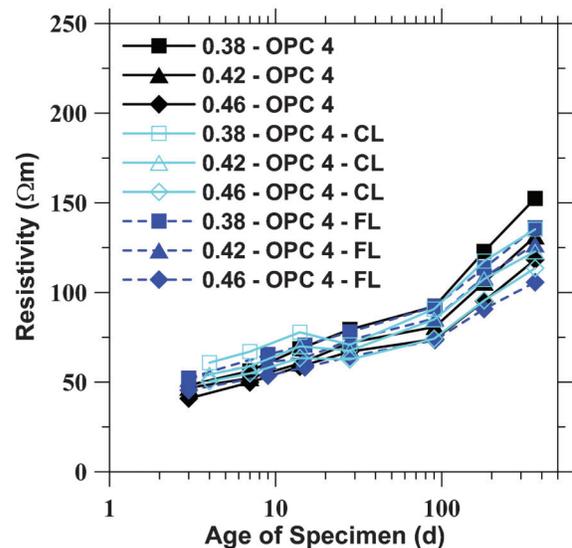


Figure 6.5 Bulk resistivity up to one year of age for OPC 4, OPC 4-CL, and OPC 4-FL at w/p of 0.38, 0.42, and 0.46.

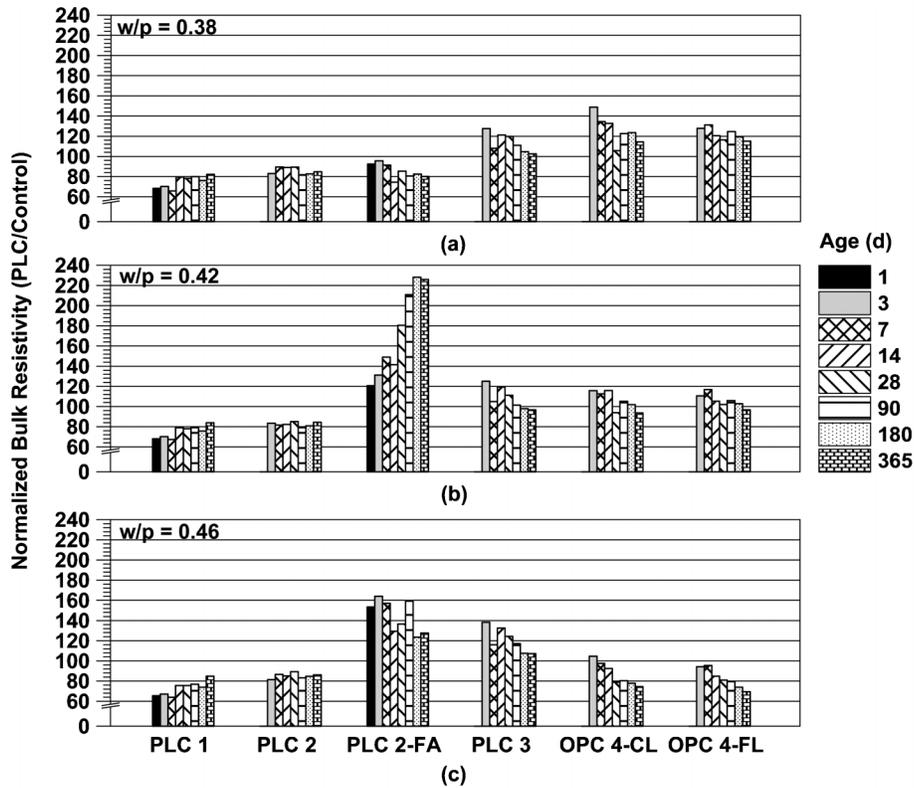


Figure 6.6 Normalized bulk resistivity of portland limestone cements with w/p of (a) 0.38, (b) 0.42, and (c) 0.46.

sorption values, final water penetration depth, and volume of permeable voids (as determined using the method outlined in ASTM C642 (61)) for each mixture are listed in Table 6.2. For this testing, the samples were stored in an environmental chamber ($50\% \pm 2\%$ RH) for a period of 12 to 14 months prior to testing, as previous research has shown that the standard conditioning process may not be adequate to ensure proper results (27). The initial DOS (after conditioning at 50%

RH) can be seen in Table 6.3, along with the change in DOS after one and eight days of water absorption testing, corresponding to plot b of Figure 6.7 through Figure 6.17. The advantage of normalizing the results by DOS (defined here as the ratio of absolute volume of absorbed water to the total volume of pores) is the ability to determine whether the specimens reach the suggested critical DOS of 88%, beyond which freeze-thaw damage can initiate (68–71).

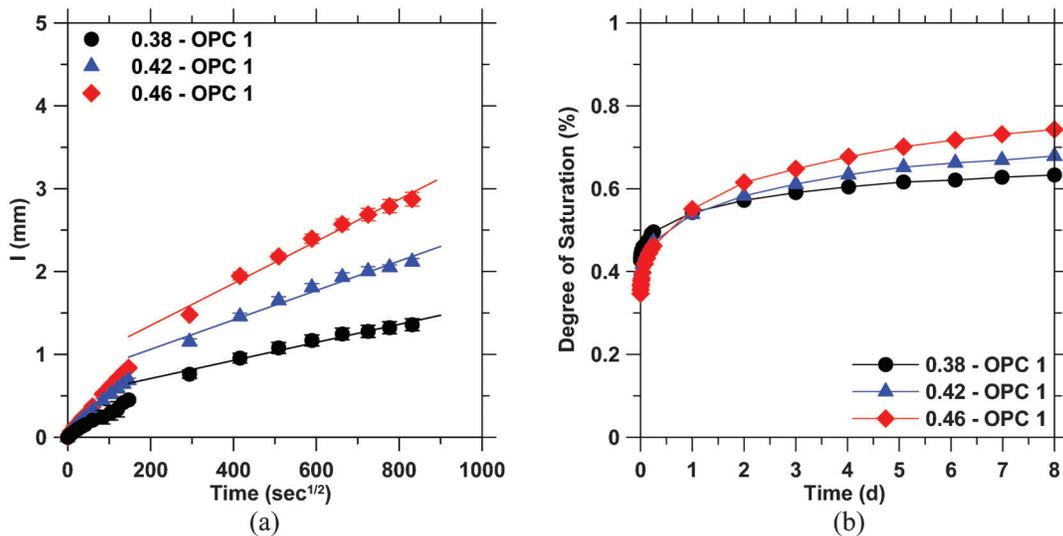


Figure 6.7 (a) water absorption and (b) change in degree of saturation for 0.38/0.42/0.46-OPC 1 mixtures.

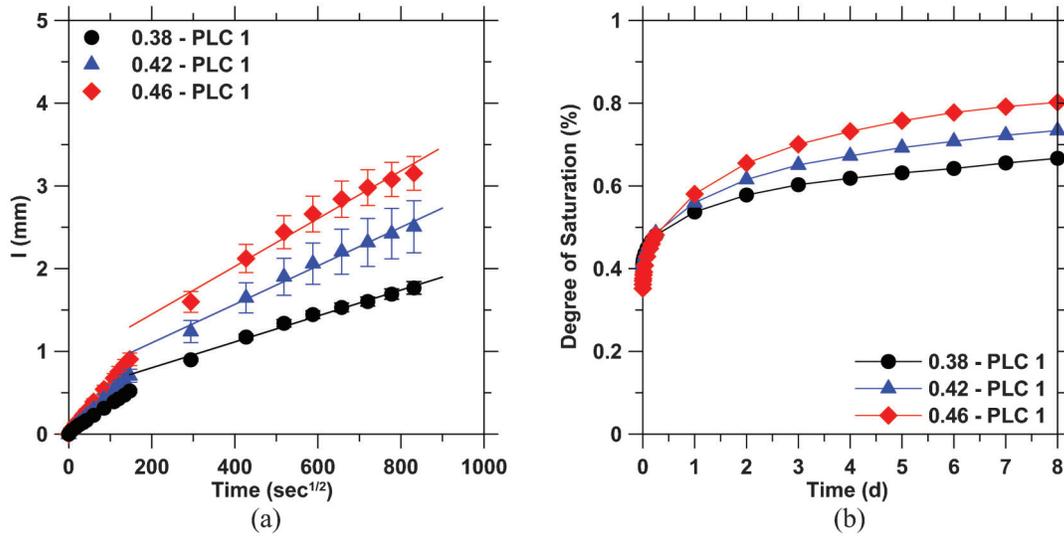


Figure 6.8 (a) water absorption and (b) change in degree of saturation for 0.38/0.42/0.46-PLC 1 mixtures.

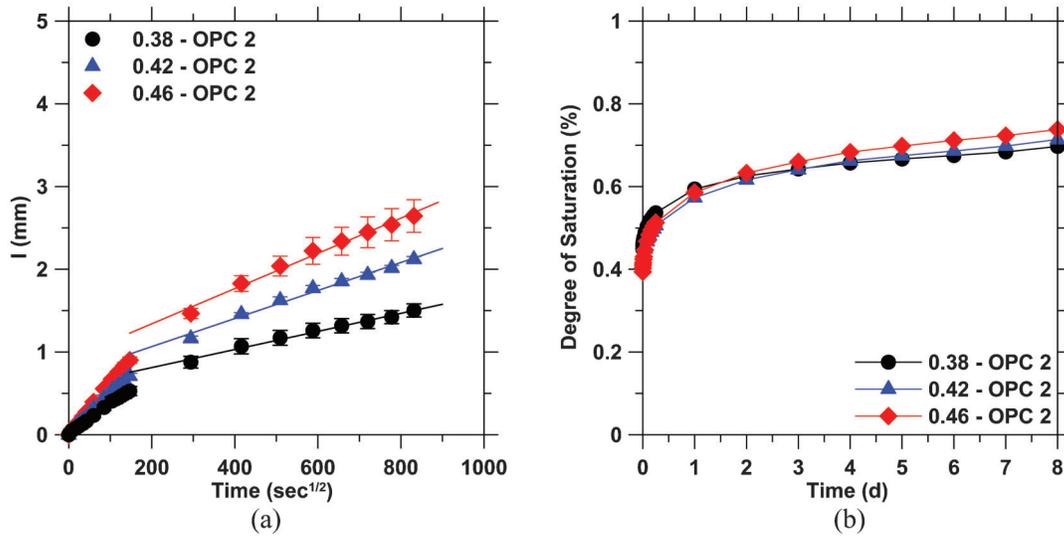


Figure 6.9 (a) water absorption and (b) change in degree of saturation for 0.38/0.42/0.46-OPC 2 mixtures.

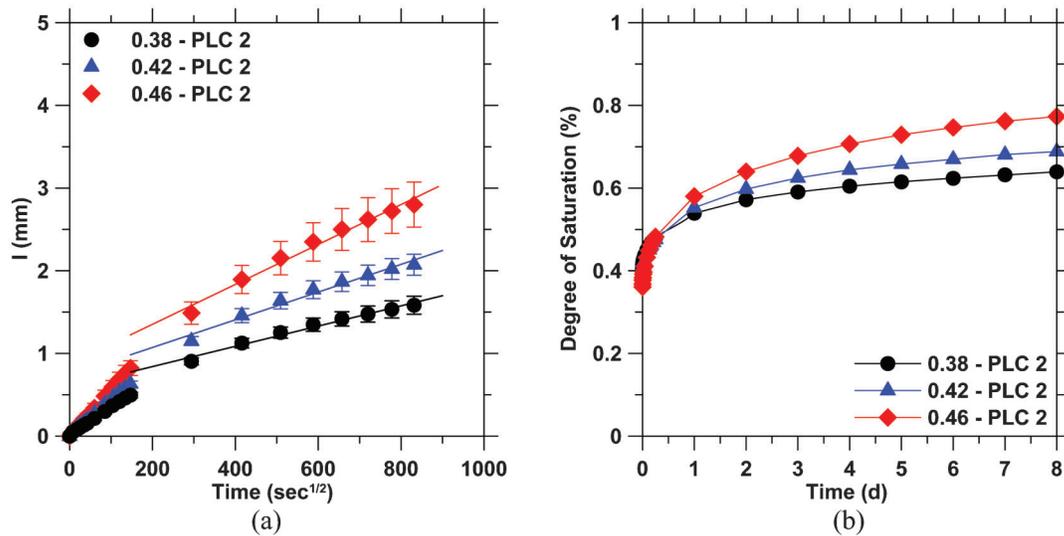


Figure 6.10 (a) water absorption and (b) change in degree of saturation for 0.38/0.42/0.46-PLC 2 mixtures.

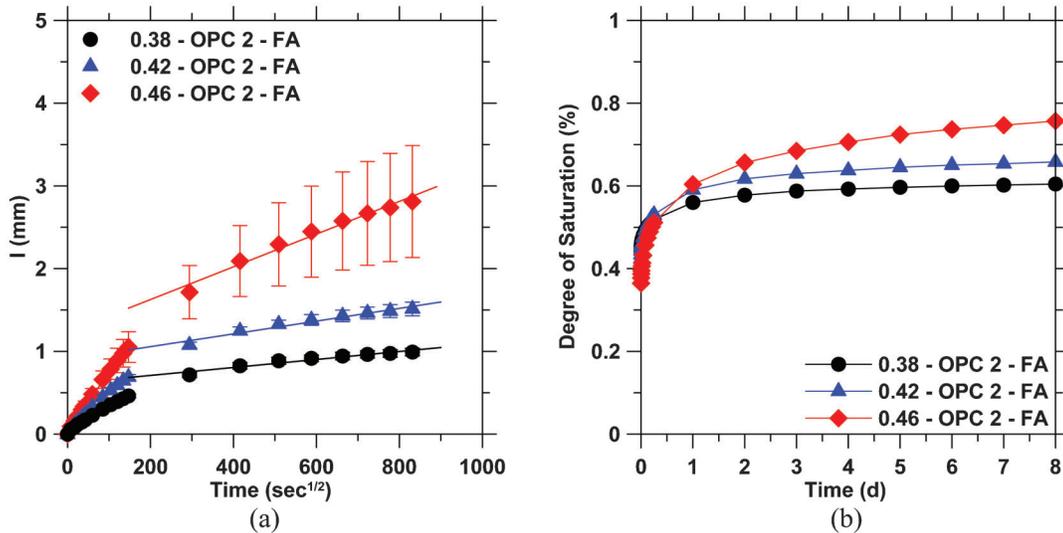


Figure 6.11 (a) water absorption and (b) change in degree of saturation for 0.38/0.42/0.46-OPC 2-FA mixtures.

A comparison of the PLC systems with their OPC counterparts shows that the PLCs have similar magnitudes of absorbed water over the duration of the testing. The initial rate of absorption varied between each of the PLCs, with PLC 1 showing a 10% increase, PLC 2 showing a 2% reduction and 20% reduction in comparison to each corresponding reference OPC. The secondary rate of absorption for each of these mixtures followed similar patterns with PLC 1 showing a 30% increase, PLC 2 showing a 10% increase, and PLC 3 showing a 30% reduction in comparison to their reference OPC. These results appear to follow the same trend as the change in the volume of permeable voids for each material, with PLC 1 and PLC 2 having 3% more voids while PLC 3 showed an average reduction in volume of voids of 5% compared to their references, however it should be noted that no air entraining admixture was used in

these mixtures. As such, any variation in the levels of air content for each mixture may have contributed to the changes in water absorption (71). Perhaps most importantly, when the water absorption results are normalized to the change in DOS, it can readily be seen that none of the PLC systems at any w/p reach the critical DOS, with the maximum DOS of any of these mixture being 82% after 8 days of absorption testing.

A comparison of the blended limestone systems (OPC 4-CL and OPC 4-FL) with their reference (OPC 4) shows an average increase of 30% in total absorbed water for each, with the secondary absorptions being noticeably more non-linear than that of OPC 4. The initial absorption increased by 18% and 26% for the OPC 4-CL and OPC 4-FL mixtures, respectively, while the secondary absorption increased by approximately 28% for each in comparison to OPC 4. In contrast to the PLC mixtures where the increase in absorption may

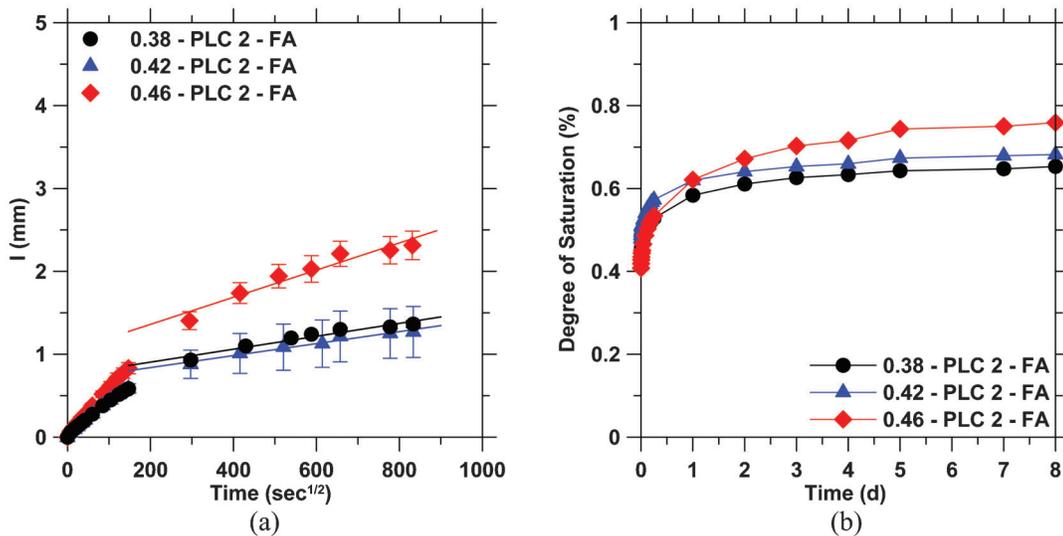


Figure 6.12 (a) water absorption and (b) change in degree of saturation for 0.38/0.42/0.46-PLC 2-FA mixtures.

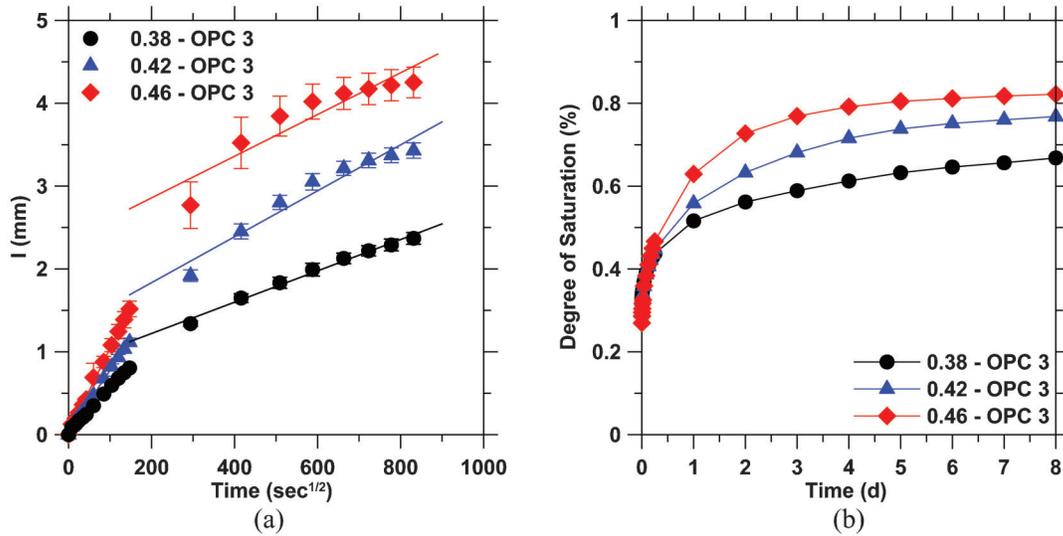


Figure 6.13 (a) water absorption and (b) change in degree of saturation for 0.38/0.42/0.46-OPC 3 mixtures.

be linked to an increase in permeable voids, the OPC 4-CL mixture showed a 4% increase in voids while the OPC 4-FL mixture had on average the same amount of voids as the OPC 4 mixture. In terms of change in DOS, neither of the blended limestone systems reached the critical degree of saturation, with 0.46-OPC 4-CL reaching 83% and 0.46-OPC 4-FL reaching 85% after 8 days of absorption testing.

A comparison of systems containing fly ash (OPC 2-FA and PLC 2-FA) with those that do not (OPC 2 and PLC 2) shows that the total absorbed water is similar ($\pm 1\%$) for each mixture except for the 0.42-PLC 2-FA system, which shows a reduction of -35%. The initial absorption of the fly ash mixtures relative to the same system without fly ash is also similar, varying by $\pm 5\%$ for each, while the secondary absorption shows

significant improvement with a -40% reduction for both the OPC 2-FA and PLC 2-FA systems. These absorptions correspond to a similar change in DOS after 8 days of testing between the PLC 2-FA and PLC 2 systems, while the change in DOS for the OPC 2-FA system shows a reduction of -15% at w/p of 0.38 and a similar change in DOS at w/p of 0.46. Comparing the OPC 2-FA mixtures with the PLC 2-FA mixture suggests that the presence of the limestone reduces the initial (-18%) and secondary absorption (-13%) at w/p of 0.42 and 0.46, however the resulting change in DOS of these systems is within 2% difference. It should be noted that the 0.38-PLC 2-FA system showed significantly higher absorption values (approximately 30% higher) than the 0.38-OPC 2-FA system, suggesting that the refinement of the pore structure in this

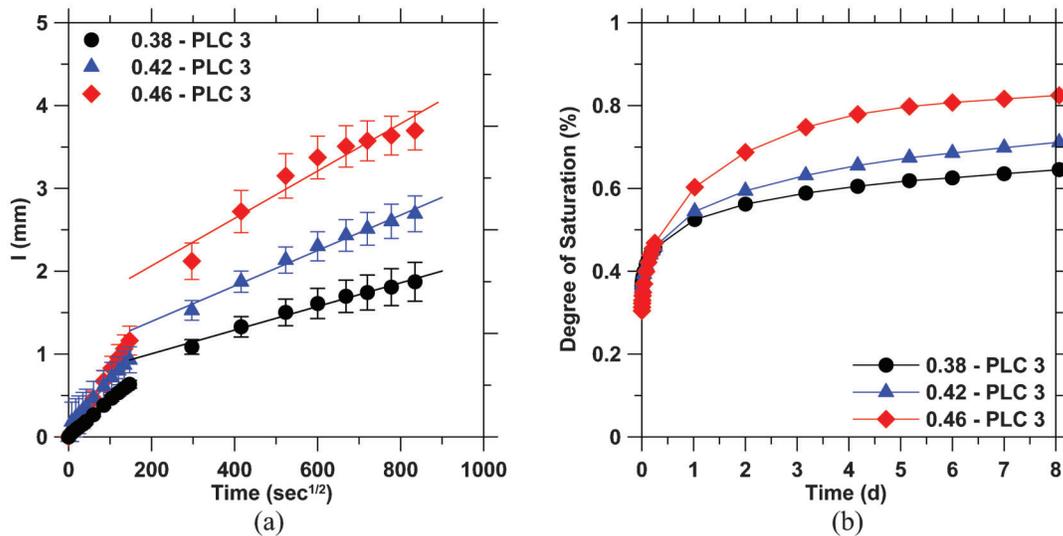


Figure 6.14 (a) water absorption and (b) change in degree of saturation for 0.38/0.42/0.46-PLC 3 mixtures.

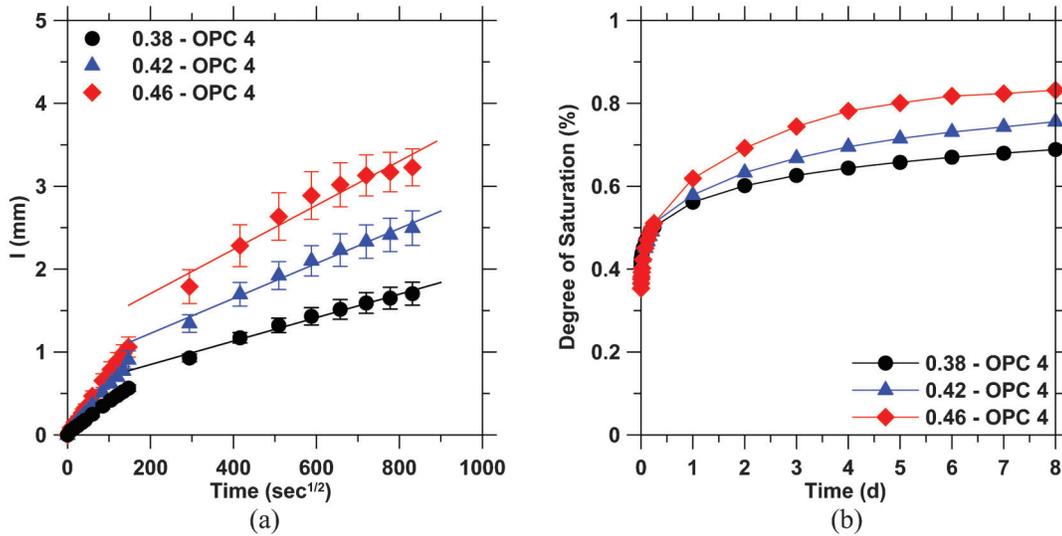


Figure 6.15 (a) water absorption and (b) change in degree of saturation for 0.38/0.42/0.46-OPC 4 mixtures.

system may have been inhibited by the presence of limestone.

6.4 Summary and Conclusions

This chapter investigated the transport properties and durability of systems containing ground limestone. The results of this chapter can be summarized as:

- The results from the migration cell testing showed that while cementitious systems containing limestone have similar volumes of permeable voids as their OPC counterparts, the chloride diffusion coefficients in these systems may range from 0 to 30% higher than the OPCs. The Stadium Lab testing indicated that this potential increase is most closely related to changes in tortuosity of these systems.
- The results from the migration cell testing indicated that both cementitious systems containing fly ash (OPC 2-FA

and PLC 2-FA) have chloride diffusion coefficients that are up to 90% lower than the same systems without fly ash (OPC 2 and PLC 2). In addition, the PLC 2-FA system showed approximately a 60% reduction in chloride diffusion coefficient when compared to the OPC 2-FA system. The Stadium Lab testing indicated that these potential reductions are most closely related to changes in tortuosity of these systems.

- The bulk resistivity of PLCs were shown to range within $\pm 25\%$ of their OPC reference mixtures. This variation may be related to changes in pore solution conductivity due to the presence of limestone in these systems, however more research is required to determine these effects.
- The bulk resistivity of the blended limestone systems (OPC 4-CL and OPC 4-FL) show a dependency on w/p, with an average increase of 25% at a w/p of 0.38 and an average reduction of 20% at a w/p of 0.46.
- The bulk resistivity of systems containing fly ash exhibit an increase of up to one order of magnitude compared to

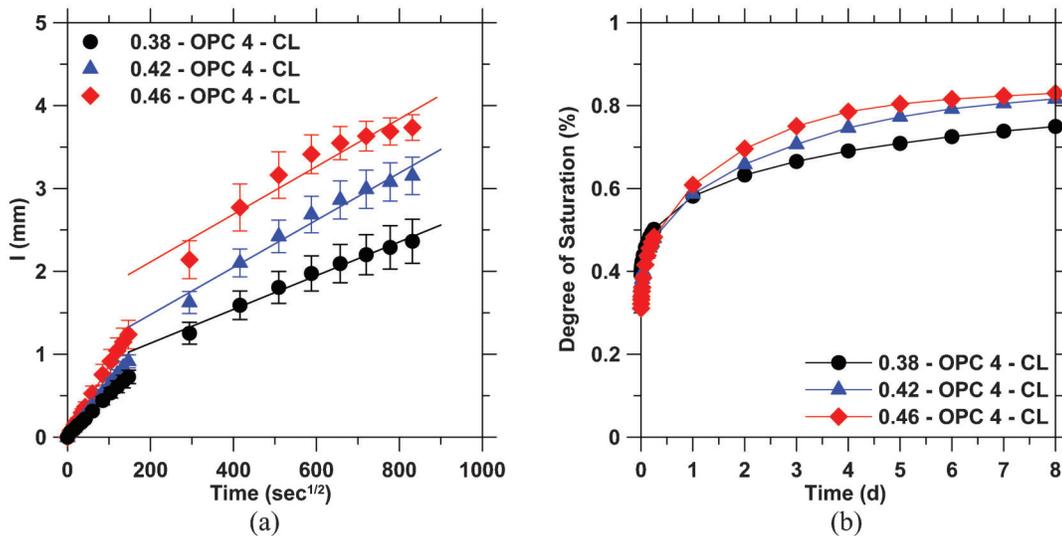


Figure 6.16 (a) water absorption and (b) change in degree of saturation for 0.38/0.42/0.46-OPC 4-CL mixtures.

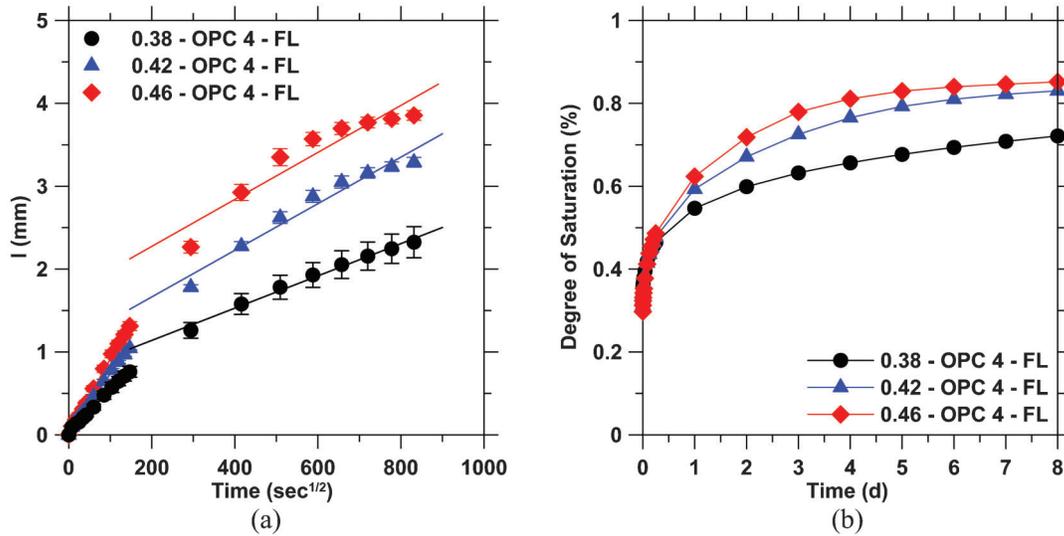


Figure 6.17 (a) water absorption and (b) change in degree of saturation for 0.38/0.42/0.46-OPC 4-FL mixtures.

TABLE 6.2

Initial and secondary sorption, depth of water penetration after eight days of absorption, and volume of permeable voids for each mixture

Mixture	S_i (mm/sec ^{1/2})	S_s (mm/sec ^{1/2})	IF (mm)	Volume of Permeable Voids (%)
0.38-OPC 1	2.84E-03	1.09E-03	1.36	0.13
0.42-OPC 1	4.60E-03	1.77E-03	2.12	0.13
0.46-OPC 1	5.65E-03	2.54E-03	2.87	0.14
0.38-PLC 1	3.42E-03	1.57E-03	1.77	0.13
0.42-PLC 1	4.73E-03	2.33E-03	2.51	0.14
0.46-PLC 1	6.09E-03	2.89E-03	3.15	0.14
0.38-OPC 2	3.58E-03	1.09E-03	1.50	0.12
0.42-OPC 2	4.81E-03	1.69E-03	2.12	0.13
0.46-OPC 2	6.20E-03	2.13E-03	2.64	0.13
0.38-OPC 2-FA	3.01E-03	4.83E-04	0.99	0.12
0.42-OPC 2-FA	4.62E-03	7.71E-04	1.51	0.13
0.46-OPC 2-FA	7.06E-03	1.98E-03	2.81	0.14
0.38-PLC 2	3.32E-03	1.22E-03	1.58	0.13
0.42-PLC 2	4.22E-03	1.67E-03	2.07	0.13
0.46-PLC 2	5.60E-03	2.41E-03	2.80	0.13
0.38-PLC 2-FA	3.90E-03	7.63E-04	1.36	0.13
0.42-PLC 2-FA	3.95E-03	7.10E-04	1.27	0.08
0.46-PLC 2-FA	5.59E-03	1.61E-03	2.31	0.13
0.38-OPC 3	5.38E-03	1.89E-03	2.37	0.13
0.42-OPC 3	7.53E-03	7.53E-03	3.43	0.14
0.46-OPC 3	1.02E-02	2.52E-03	4.25	0.15
0.38-PLC 3	4.33E-03	1.43E-03	1.87	0.13
0.42-PLC 3	5.78E-03	2.14E-03	2.69	0.14
0.46-PLC 3	8.02E-03	2.86E-03	3.70	0.14
0.38-OPC 4	3.79E-03	1.41E-03	1.70	0.12
0.42-OPC 4	5.83E-03	2.11E-03	2.49	0.13
0.46-OPC 4	7.23E-03	2.66E-03	3.23	0.13
0.38-OPC 4-CL	4.90E-03	2.04E-03	2.36	0.13
0.42-OPC 4-CL	6.27E-03	2.85E-03	3.15	0.13
0.46-OPC 4-CL	8.57E-03	2.88E-03	3.74	0.14
0.38-OPC 4-FL	5.07E-03	1.95E-03	2.33	0.12
0.42-OPC 4-FL	7.03E-03	2.81E-03	3.29	0.13
0.46-OPC 3-FL	8.96E-03	2.83E-03	3.85	0.14

TABLE 6.3
Degree of saturation after at equilibrium with 50% RH and associated increase in degree of saturation after 1 and 8 days of water absorption

Mixture	Degree of Saturation (%)		
	Initial: 50% Relative Humidity	1 d	8 d
	0.38-OPC 1	0.43	0.54
0.42-OPC 1	0.37	0.54	0.68
0.46-OPC 1	0.35	0.55	0.74
0.38-PLC 1	0.40	0.54	0.67
0.42-PLC 1	0.39	0.56	0.73
0.46-PLC 1	0.35	0.58	0.80
0.38-OPC 2	0.45	0.59	0.70
0.42-OPC 2	0.40	0.57	0.71
0.46-OPC 2	0.38	0.59	0.74
0.38-OPC 2-FA	0.44	0.56	0.60
0.42-OPC 2-FA	0.42	0.59	0.66
0.46-OPC 2-FA	0.36	0.60	0.76
0.38-PLC 2	0.41	0.54	0.64
0.42-PLC 2	0.38	0.55	0.69
0.46-PLC 2	0.36	0.58	0.77
0.38-PLC 2-FA	0.43	0.58	0.65
0.42-PLC 2-FA	0.48	0.62	0.68
0.46-PLC 2-FA	0.41	0.62	0.76
0.38-OPC 3	0.32	0.52	0.67
0.42-OPC 3	0.29	0.56	0.77
0.46-OPC 3	0.27	0.63	0.82
0.38-PLC 3	0.36	0.52	0.65
0.42-PLC 3	0.33	0.54	0.71
0.46-PLC 3	0.30	0.60	0.82
0.38-OPC 4	0.41	0.56	0.69
0.42-OPC 4	0.37	0.58	0.76
0.46-OPC 4	0.35	0.62	0.83
0.38-OPC 4-CL	0.39	0.58	0.75
0.42-OPC 4-CL	0.34	0.59	0.82
0.46-OPC 4-CL	0.31	0.61	0.83
0.38-OPC 4-FL	0.34	0.55	0.72
0.42-OPC 4-FL	0.31	0.59	0.83
0.46-OPC 3-FL	0.30	0.62	0.85

systems without fly ash, with the presence of limestone (PLC 2-FA) further improving the bulk resistivity at w/p above 0.42 compared to the OPC 2-FA mixture.

- The initial and secondary rates of absorption for the PLCs varied within $\pm 30\%$ of the reference OPCs, while the blended limestone systems showed an average increase of up to 30% compared to their reference.
- Each mixture tested remained below the critical degree of saturation of 88% after 8 days of absorption testing.

7. SUMMARY AND RECOMMENDATIONS

7.1 Introduction

Portland limestone cements (PLCs) have been engineered in North America (following ASTM C 595/ASTM M240) specifically to achieve similar performance in comparison to their ordinary portland cement (OPC) counterparts. This report investigates the PLC (interground limestone-clinker-sulfate) systems and compares them with the OPC (clinker-sulfate)

made using the same clinker. In addition, systems were investigated where limestone was added to and blended to the conventional OPC.

7.2 Summary of Experimental Studies

Chapter 3 characterized the physical and chemical properties of the cementitious materials used in this study. It was observed that the intergrinding of the limestone with clinker in the PLC is primarily a physical process that does not appear to result in any chemical alterations. The commercially available PLCs were observed to contain approximately 10% to 14% of limestone. Intergrinding the limestone with the clinker results in a finer powder with a reduction in the coarser particles ($>20 \mu\text{m}$) and an increase in fine limestone particles. When the limestone is blended with OPC, the resulting particle size distribution has additional particles the size of the added limestone but no reduction in coarser particles. The specific surface area (Blaine fineness) of the PLC was observed to increase by 10% to 30% in comparison to the corresponding OPC. This increased fineness is generally done to reduce the effects of dilution. SEM images were captured and showed that for the PLC system the limestone is ground finer than the cement.

Chapter 4 used isothermal calorimetry, chemical shrinkage and thermogravimetric analysis to assess the hydration reaction of the OPC, PLC, and OPC blended limestone systems.

Generally the PLC mortars exhibited a greater heat release than the OPC after 7 days of curing. This corresponds with the PLC having a degree of hydration that met or exceeded the degree of hydration of the OPC system. The blended OPC-limestone systems (OPC 4-CL and OPC 4-FL) both exhibited lower heat released at early ages, corresponding to a similar degree of hydration for the fine limestone system and a 10% reduction in the coarse limestone system in comparison to OPC 4. The chemical shrinkage indicated a higher level of hydration in the PLC mortars compared to the OPCs. The chemical shrinkage of the blended limestone systems also showed an increase in chemical shrinkage, with negligible difference due to the size of the limestone particles. The calorimetry and chemical shrinkage results imply that these PLC materials would be able to be used interchangeably with OPC in practice as it relates to the rate of reaction. The blended systems would need to be evaluated due to the influence of particle size.

The PLC mortars exhibited relatively similar activation energies compared to the corresponding OPCs. This would allow the maturity method to be used by INDOT for both the PLC and OPC systems.

All cementitious systems containing limestone showed a stronger monocarbonate peak than the corresponding OPCs, especially at ages of 28 days or more. Additionally, the presence of fly ash resulted in the formation of significantly more monocarbonate in the PLC pastes. This suggests that INDOT should consider

the benefit of using PLC with fly ash due to their synergistic effects.

Chapter 5 investigated the mechanical properties of OPC, PLC and OPC-Limestone blends of up to 15%. Tests were performed to assess the time of set, the modulus of elasticity, compressive strength, flexural strength, drying shrinkage, and restrained autogenous shrinkage.

The time of set for the PLCs was on average 10% earlier than OPCs, while the time of set of blended limestone systems is dependent on the particle size of limestone used with the fine limestone accelerating set and the coarse limestone delaying set.

Generally, the PLCs show an increase in compressive strength at early ages that diminishes with time, resulting in similar compressive strengths at 28 days of age. The OPC-blended limestone cements had an average reduction in strength of 8.5% with greater losses at higher w/p. In general the elastic modulus of the OPC and PLC system is similar. There is a slight reduction in modulus of elasticity for the PLC which was more evident at lower w/p. The flexural strength of the PLCs at 7 days of age was similar to the OPCs at all w/p tested. The flexural strength of the blended OPC-limestone cements showed increasing reductions in flexural strength with both increasing w/p and limestone particle size.

No significant change in drying shrinkage or restrained shrinkage cracking was observed for the PLC 2 cement. Although no tests were performed here, it should be noted that previous studies (Bucher et al., 2008) have shown that systems with fine inclusions (such as the blended limestone cements) have shown increased susceptibility to shrinkage and cracking.

The transport properties tested include the chloride diffusion coefficients as determined through Stadium Lab, the bulk electrical resistivity, and the rate of water absorption with associated change in degree of saturation.

The results from the migration cell testing showed that while cementitious systems containing limestone have similar volumes of permeable voids as their OPC counterparts, the chloride diffusion coefficients in these systems may range from 0% to 30% higher than the OPCs. The results from the migration cell testing indicated that both cementitious systems containing fly ash (OPC 2-FA and PLC 2-FA) have chloride diffusion coefficients that are up to 90% lower than the same systems without fly ash (OPC 2 and PLC 2). In addition, the PLC 2-FA system showed an approximate 60% reduction in chloride diffusion coefficient when compared to the OPC 2-FA system.

The bulk resistivity of PLCs were shown to range within $\pm 25\%$ of their OPC references mixtures. This variation may be related to changes in pore solution conductivity due to the presence of limestone in these systems, however more research is required to determine these effects. The bulk resistivity of the blended limestone systems (OPC 4-CL and OPC 4-FL) show a dependency on w/p, with an average increase of 25% at

a w/p of 0.38 and an average reduction of -20% at a w/p of 0.46. The bulk resistivity of systems containing fly ash exhibit an increase of up to one order of magnitude compared to systems without fly ash, with the presence of limestone (PLC 2-FA) further improving the bulk resistivity at w/p above 0.42 compared to the OPC 2-FA mixture.

The initial and secondary rates of absorption for the PLCs varied within $\pm 30\%$ of the reference OPCs, while the blended limestone systems showed an average increase of up to 30% compared to their reference.

It is worth noting that research is still being conducted to assess the potential influence of sulfates and deicing salts on the relative performance of OPC and PLC systems.

7.3 Impact on Structural Design for Pavements

The intent of introducing portland limestone cements (PLCs) under ASTM C595 is to address the growing concerns of sustainability in cement and concrete production by providing a replacement for ASTM C150 Type I/II ordinary portland cements (OPCs) that achieves similar performance while reducing clinker content. As such, the implementation of these materials is subject to the present engineering design practice, which focuses on the strength of materials and the prediction of these properties using codified equations. To address these concerns, the following series of figures were prepared. Figure 7.1 shows the compressive strength of the cementitious systems containing limestone plotted against each material's OPC counterpart. The dashed line on the plot shows a one-to-one relationship, while the solid lines indicate $\pm 10\%$. As it can readily be seen, these mixtures containing limestone fall mostly within 10% of a one-to-one strength ratio of strength in comparison to the OPC system they are intended to replace. Figure 7.2 shows the modulus of

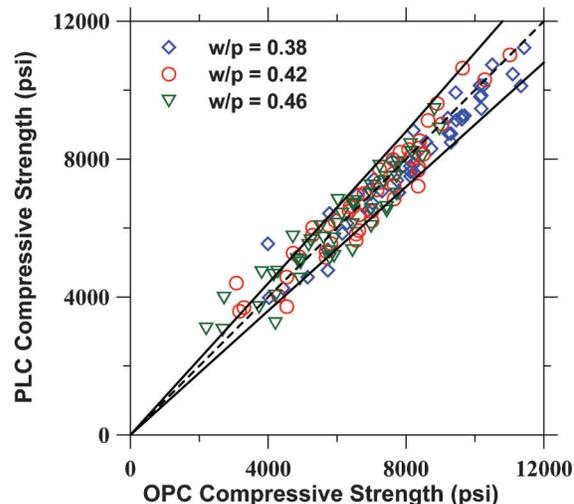


Figure 7.1 PLC compressive strength plotted versus each mixture's reference OPC. The dashed line indicates a 1:1 relationship, while the solid lines indicate $\pm 10\%$.

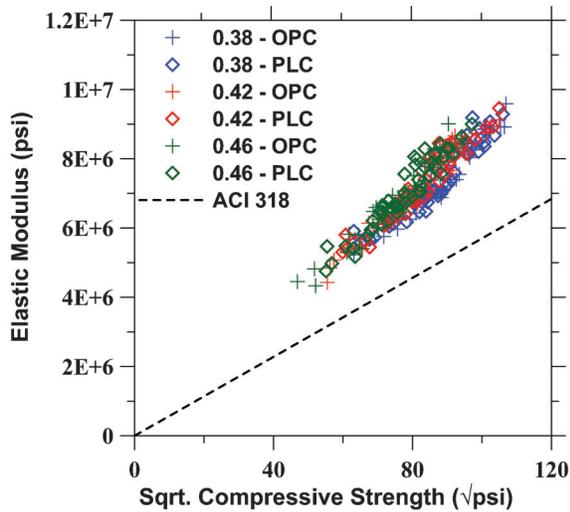


Figure 7.2 Elastic modulus of each concrete mixture tested. The dashed line indicates the result from ACI 318, Section 8.5.1.

elasticity for each concrete mixture tested, with the dashed line on the plot indicating the result of ACI 318, Section 8.5.1. The results indicate a close relationship of modulus of elasticity between OPCs and PLCs, while all mixtures lie well above the ACI 318 equation. Figure 7.3 shows the flexural strength as a function of the square root of compressive strength for each concrete mixture tested, with the dashed line indicating the result of Equation (9-10) in ACI 318. As it can readily be seen, each of the mixtures tested lie well above the code equation. These results collectively indicate that the use of PLC instead of OPC will have minimal effect on the rate of reaction, time of set, or mechanical properties for use in the design of transportation structures with this material.

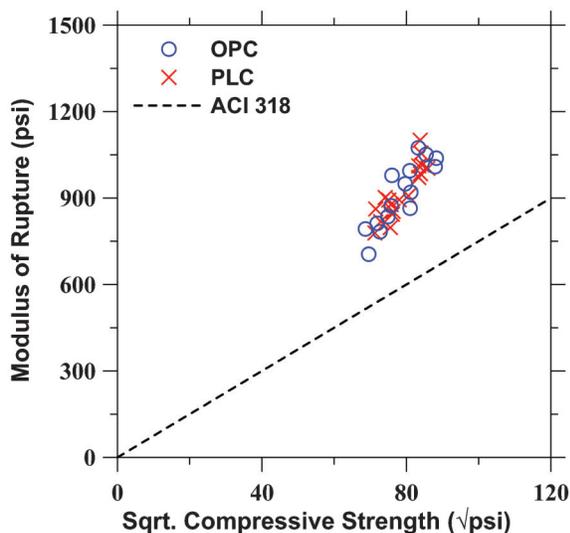


Figure 7.3 Flexural strength of each concrete mixture tested. The dashed line indicates the result from ACI 318, Equation (9-10).

7.4 Overall Recommendation

It has been observed that in general the PLC and OPC systems have similar hydration, set, and mechanical performance. Transport properties in this study show behavior that is $\pm 30\%$ of the conventional OPC system depending on the system. Literature has shown similar freeze-thaw resistance when these materials are used in properly air entrained mixtures. Results for fly ash with PLC systems suggest synergistic benefits and should be investigated further. Based on this it appears that PLC that meets ASTM C 595/AASHTO M240 should be considered for a potential field trial when locally available.

INDOT is encouraged to follow research that is being conducted to assess the potential influence of sulfates and deicing salts on the relative performance of OPC and PLC systems. Unless something negative is observed from the sulfate or deicing salt studies PLC (ASTM C595, AASHTO M240) should be able to be used interchangeably with OPC.

7.5 Expected Benefits

The expected benefits of implementing the use of PLCs is two-fold. The overall objective of utilizing PLCs is to decrease the amount of clinker necessary for the production of one unit volume of concrete. The implications of reducing the amount of clinker necessary to produce concrete can lead to cost savings and reductions in CO₂ emissions. Recent studies have indicated that the use of PLCs containing up to 15% of interground limestone has the potential to reduce CO₂ emissions by up to 15% (31).

In addition to these two primary benefits, the production of PLCs can also lead to an extended life of limestone quarries. In the production of PLCs, a portion of the limestone is being ground in lieu of calcining to produce cement. The calcination process of limestone results in a reduction in mass of more than 40% when CO₂ is liberated from the limestone. In contrast to this, grinding the limestone results in no significant mass lost. The result is a more efficient use of limestone in the production of cement and a net reduction in the mass of limestone required to produce PLCs.

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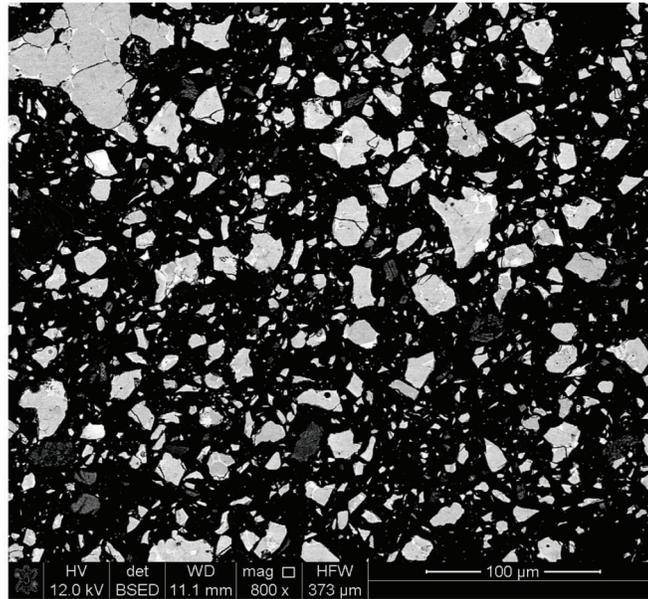
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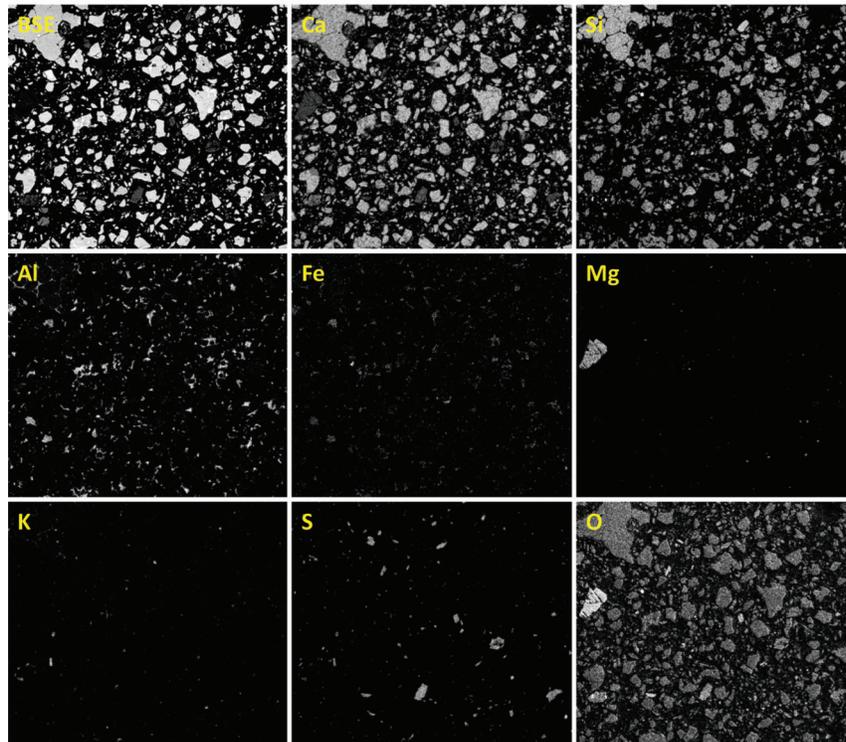
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APPENDIX. BSE AND ELEMENT MAPPING RESULTS

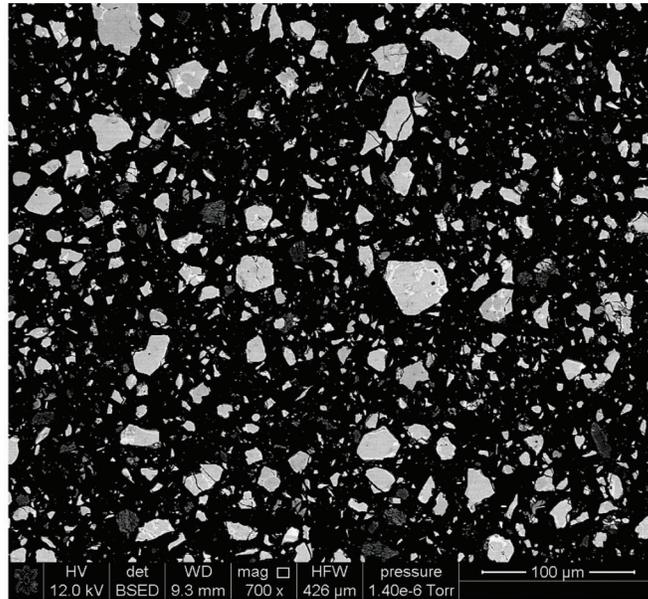


(a)

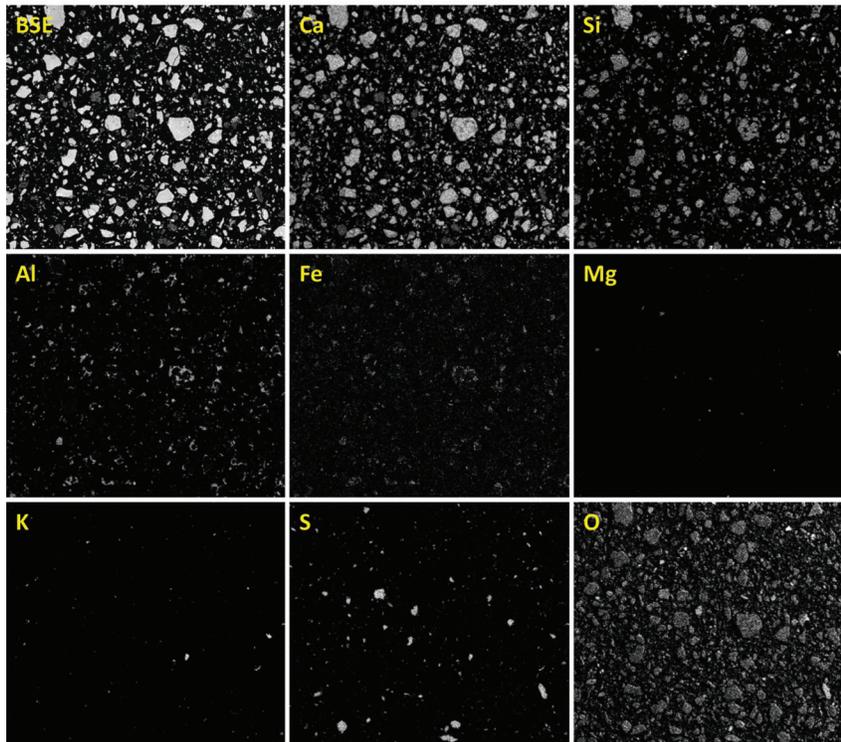


(b)

Figure A.1 Backscattered electron imaging (a) and element mapping (b) for OPC 1.

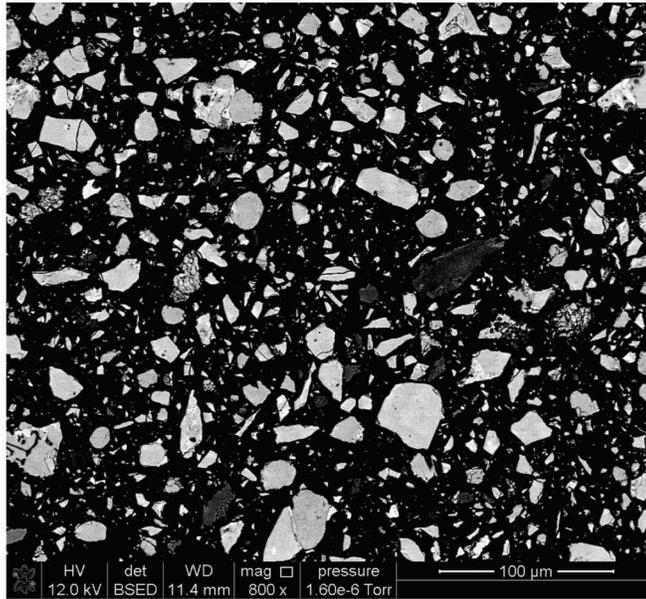


(a)

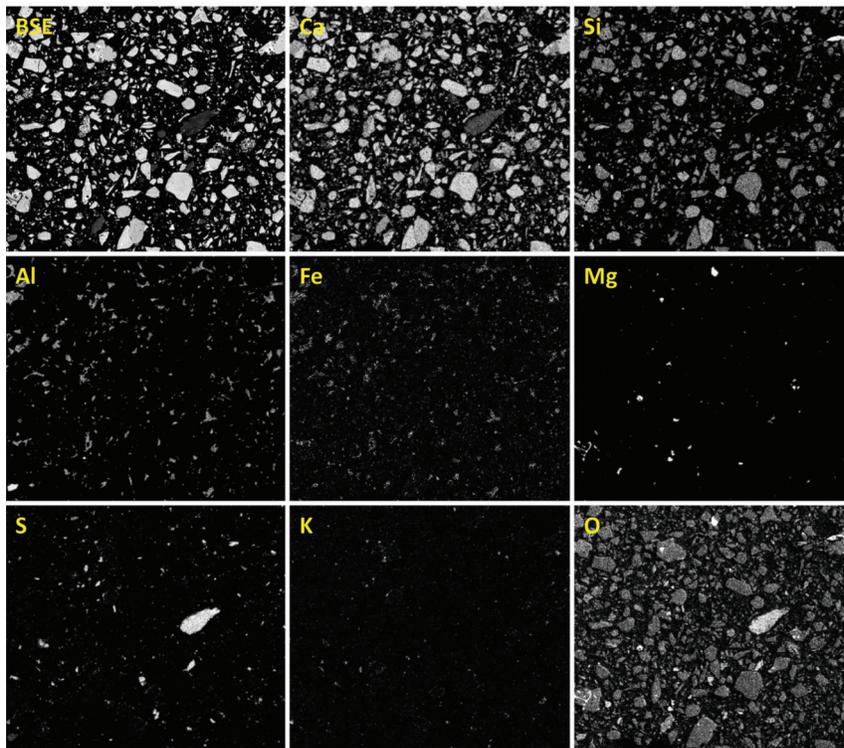


(b)

Figure A.2 Backscattered electron imaging (a) and element mapping (b) for PLC 1.

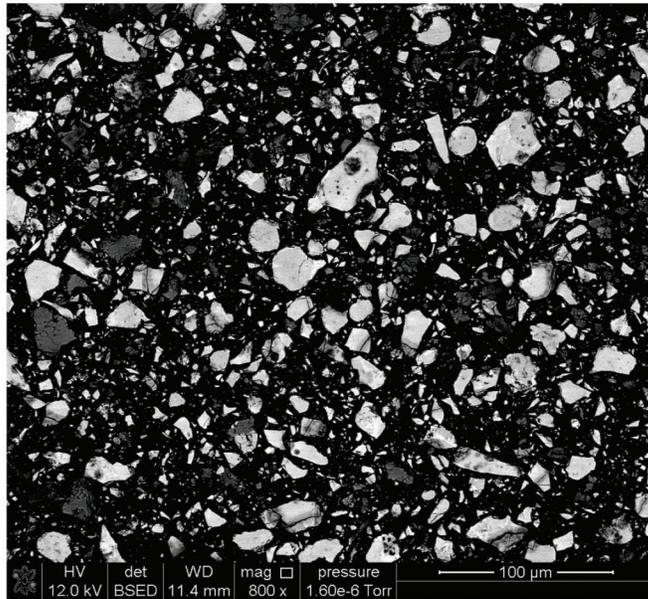


(a)

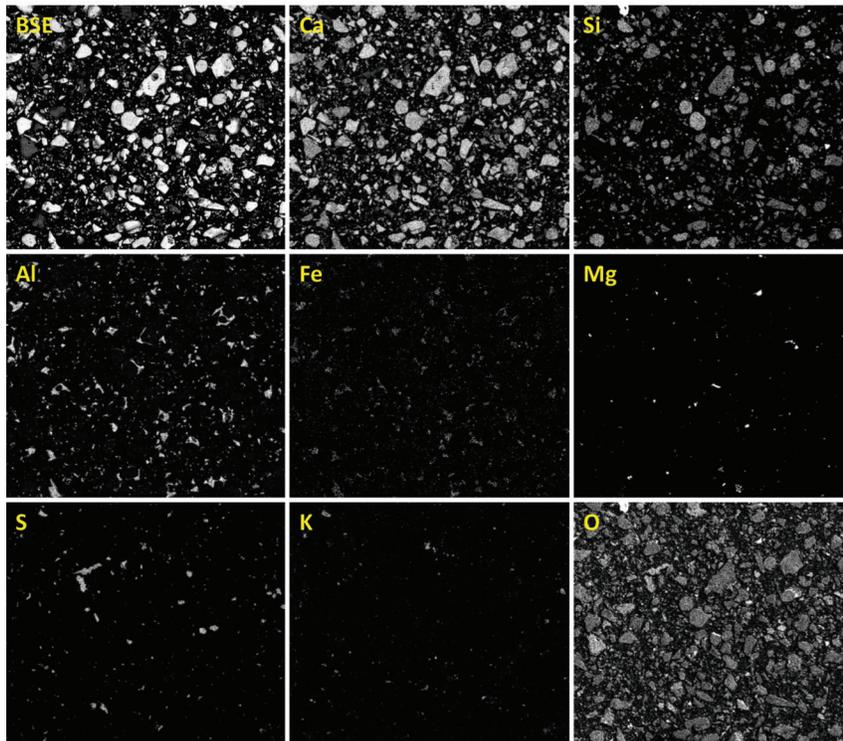


(b)

Figure A.3 Backscattered electron imaging (a) and element mapping (b) for OPC 2.

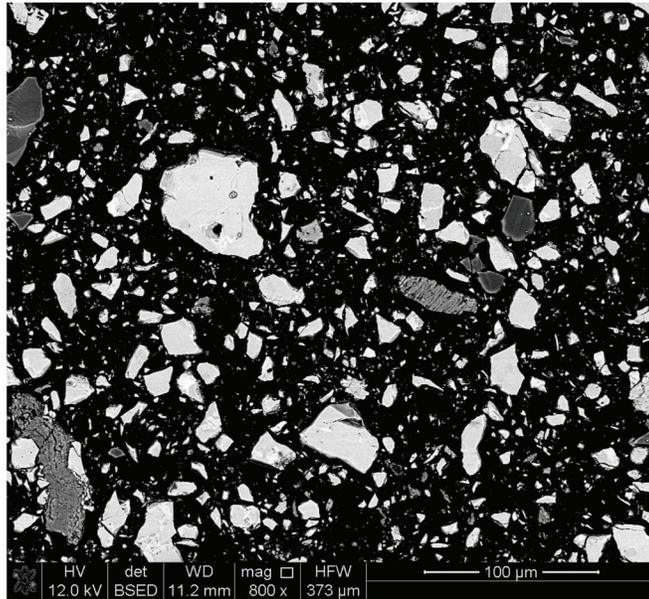


(a)

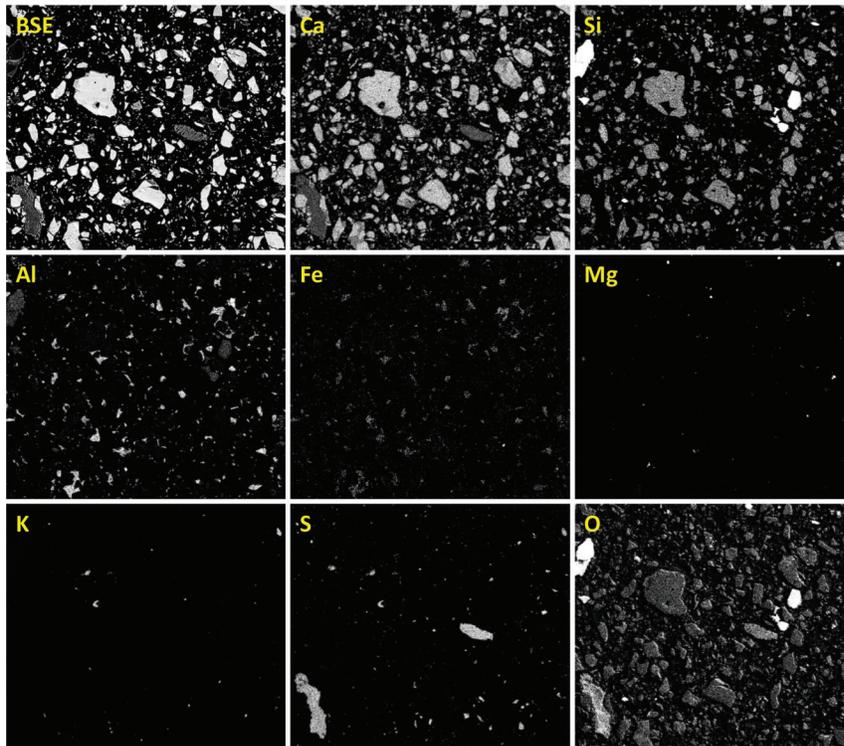


(b)

Figure A.4 Backscattered electron imaging (a) and element mapping (b) for PLC 2.

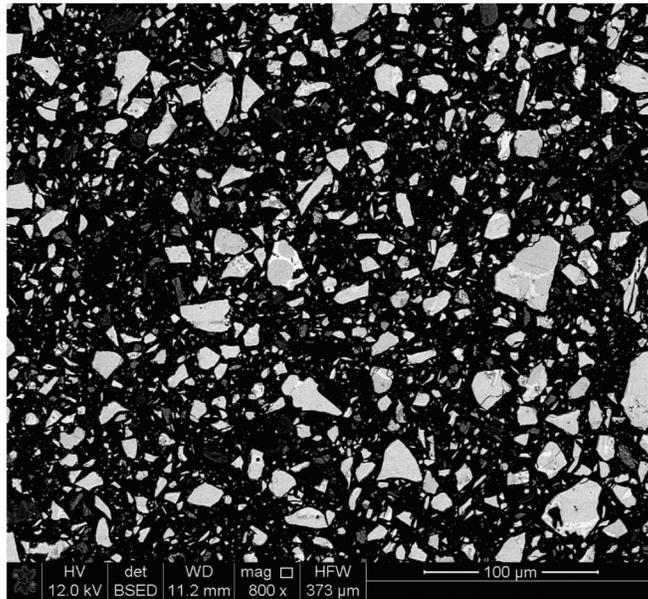


(a)

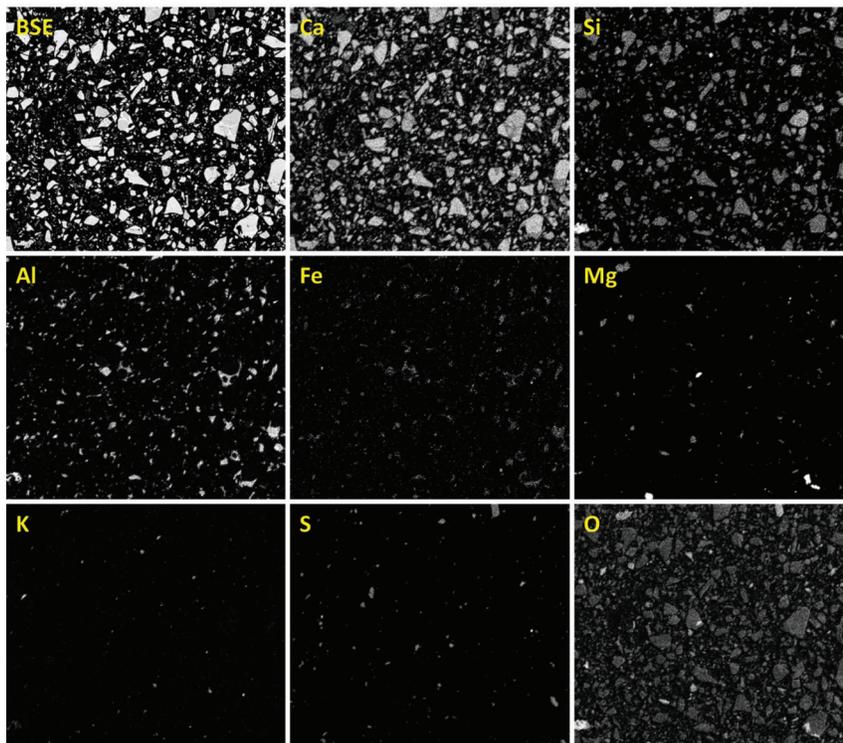


(b)

Figure A.5 Backscattered electron imaging (a) and element mapping (b) for OPC 3.

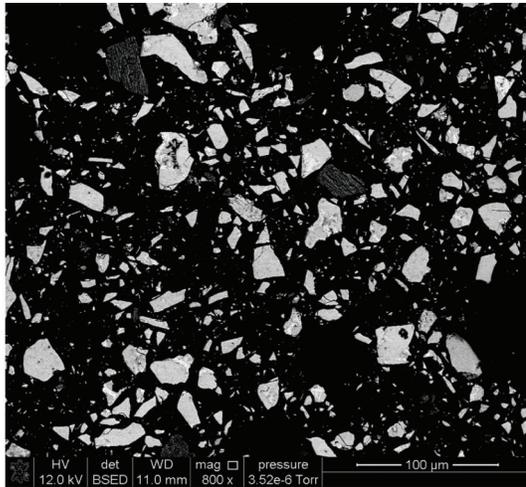


(a)

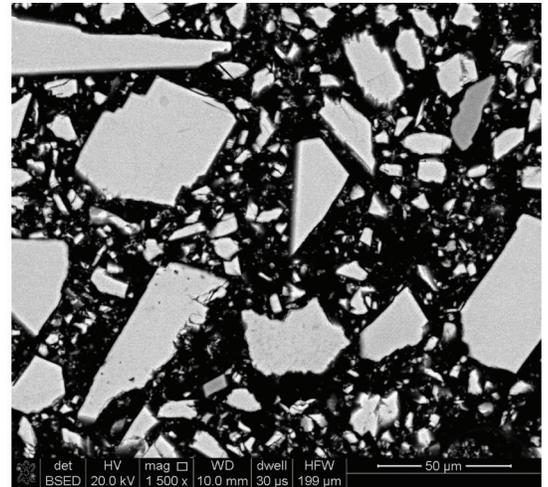


(b)

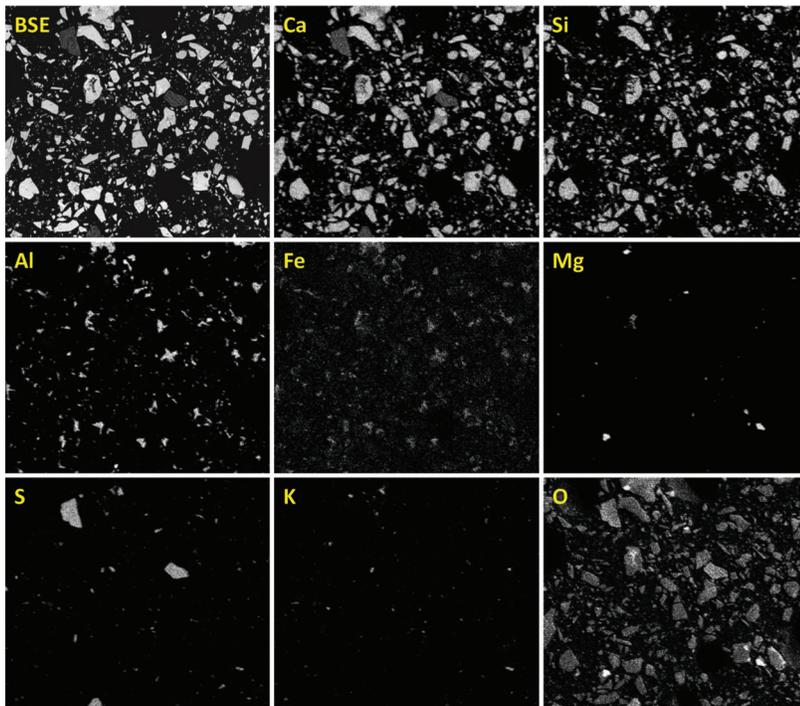
Figure A.6 Backscattered electron imaging (a) and element mapping (b) for PLC 3.



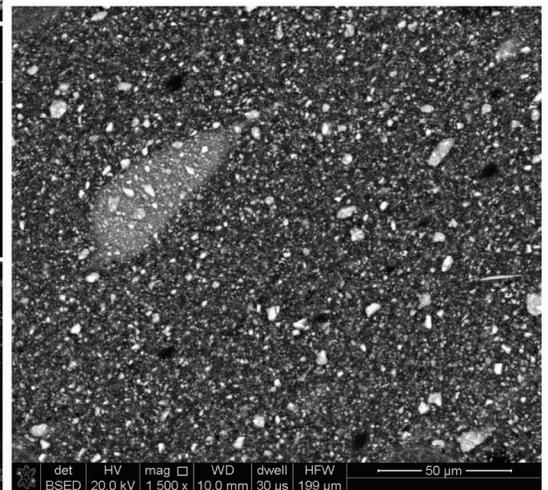
(a)



(c)

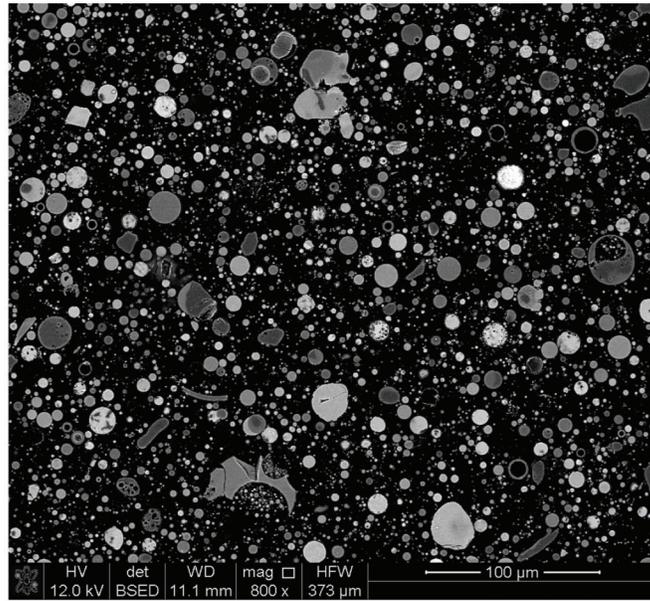


(b)

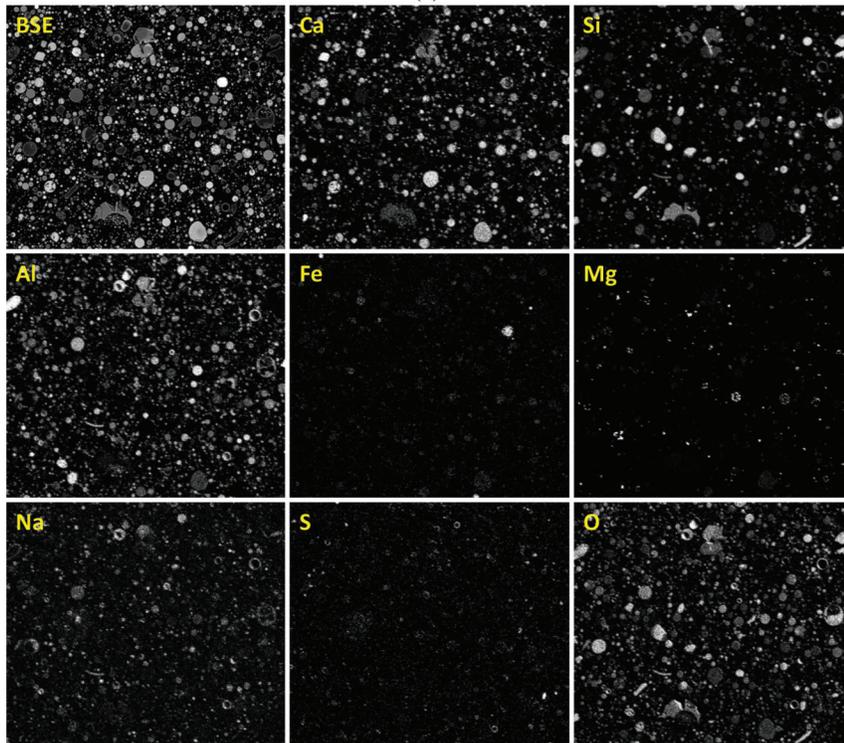


(d)

Figure A.7 Backscattered electron imaging (a) and element mapping (b) for OPC 4 and backscattered electron imaging for CL (c) and FL (d).



(a)



(b)

Figure A.8 Backscattered electron imaging (a) and element mapping (b) for FA.

About the Joint Transportation Research Program (JTRP)

On March 11, 1937, the Indiana Legislature passed an act which authorized the Indiana State Highway Commission to cooperate with and assist Purdue University in developing the best methods of improving and maintaining the highways of the state and the respective counties thereof. That collaborative effort was called the Joint Highway Research Project (JHRP). In 1997 the collaborative venture was renamed as the Joint Transportation Research Program (JTRP) to reflect the state and national efforts to integrate the management and operation of various transportation modes.

The first studies of JHRP were concerned with Test Road No. 1—evaluation of the weathering characteristics of stabilized materials. After World War II, the JHRP program grew substantially and was regularly producing technical reports. Over 1,500 technical reports are now available, published as part of the JHRP and subsequently JTRP collaborative venture between Purdue University and what is now the Indiana Department of Transportation.

Free online access to all reports is provided through a unique collaboration between JTRP and Purdue Libraries. These are available at: <http://docs.lib.purdue.edu/jtrp>

Further information about JTRP and its current research program is available at: <http://www.purdue.edu/jtrp>

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