GEORGIA DOT RESEARCH PROJECT 16-16 FINAL REPORT

Evaluation of Metakaolin and Slag for GDOT Concrete Specifications and Mass Concrete Provision - Phase I



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GDOT Research Project 16-16

Final Report

Evaluation of Metakaolin and Slag for GDOT Concrete Specifications and Mass Concrete Provision – Phase I

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EXECUTIVE SUMMARY

With the availability of kaolin in middle Georgia, GDOT can take advantage of this material to improve the overall properties of concrete mixtures and decrease demand for cement and fly ash.. This report documents the evaluation of (a) three metakaolin products, (b) two slag products, and (c) three combined slag and metakaolin products as binary or ternary replacements for cement. Nineteen supplementary cementitious mixtures, including the control, are studied to evaluate mechanical and durability properties by conducting various tests.

The tests include the measurements of (1) coefficient of thermal expansion, (2) rapid chloride permeability, (3) compressive strength, (4) splitting tensile strength, (5) modulus of elasticity, (6) modulus of rupture, (7) alkali-silica reactivity, (8) sulfate expansion, (9) dry shrinkages, and (10) heat of hydration.

This report on the Phase-I project presents the findings of six mixtures, including one of the three metakaolin products. A comprehensive analysis of the overall results with findings from two additional metakaolin products will be presented as a part of the Phase-II report (RP 16-30).

Based on the findings of this evaluation, it is recommended that:

- Optimum cement replacement with metakaolin should range between 10% and 15%.
- Ternary mixtures with 45% cement replacement (15% metakaolin and 30% slag) should be considered for reducing the heat of hydration in mass concrete mixtures.
- Synthesis of the overall results should be made to comprehensively understand the benefits of using metakaolin in both binary and ternary replacement mixtures.

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This report presents a portion of Matthew Sullivan's (pending) MS thesis. Matthew dedicated his time to conducting various tests that yielded the findings and recommendations presented herein. The heat of hydration curves were generated by Hiwa Hamid, a PhD student at the University of Georgia.

ABBREVIATIONS LIST

Abbreviation

AASHTO American Association of State Highway and Transportation Officials

ACT Advanced Cement Technology Inc.

ASR Alkali-Silica Reactivity

CTE Coefficient of Thermal Expansion

DEF Delayed Ettringite Formation

DOT Department of Transportation

FA Fly Ash

GDOT Georgia Department of Transportation

GGBFS Ground Granulated Blast Furnace Slag

HoH Heat of Hydration

ITZ Interfacial Transition Zone

MK Metakaolin

MOE Modulus of Elasticity

MOR Modulus of Rupture

PCE Poly-carboxylate Ether

RCP Rapid Chloride Permeability

RCPT Rapid Chloride Permeability Test

SF Silica Fume

SL Slag

SSD Saturated Surface-Dry

TRB Transportation Research Board

1. INTRODUCTION

1.1 Background

A pozzolan is a siliceous or alumino-siliceous material that in finely divided form and in the presence of moisture chemically reacts with the calcium hydroxide released by the hydration of Portland cement to form calcium silicate hydrate and other cementitious compounds. Pozzolans and slags are generally categorized as supplementary cementitious materials or mineral admixtures [1]. The most common natural pozzolans used today are processed materials, which are heat treated in a kiln and then ground to a fine powder; they include calcined clay, calcined shale, and metakaolin. Metakaolin, a special calcined clay, is produced by low temperature calcination of high purity kaolin clay. The product is ground to an average particle size of 1–2 micrometers [1].

When metakaolin is used as a partial cement replacement, improved performance has been observed, such as increased strength and reduced permeability [2]. Marikunte and Phelps statistically demonstrated that replacing cement with metakaolin contributed more to concrete achieving high performance than reducing water content. San Nicolas et al. [3] concluded that the substitution by metakaolin (25% by weight) improves the durability of concrete. Ferreira et al. [4] reported on the improved strength, durability properties, and chloride penetration resistance of concrete with metakaolin. Khatib et al. [5] found that the use of metakaolin with fly ash as a cement replacement reduced concrete shrinkage. Lagier and Kurtis [6] reported metakaolin use accelerated the hydration process as a result of its higher surface area, though, Brykov et al. [7] found that this rate depends on metakaolin dosage.

Due to its increased durability, highly reactive metakaolin is widely used for concrete overlay design by Illinois, Iowa, and a few other state DOTs. Despite frequent use and positive responses to metakaolin in concrete mixtures in the literature, no comprehensive study to date has examined its use and established limits in GDOT's various concrete classes.

Advantages of using metakaolin as a partial cement replacement:

Increased compressive and flexural strengths

- Increased resistance to chemical attack and durability
- Enhanced workability
- o Improved color by lightening the color of concrete
- o Reduced effects of alkali-silica reactivity (ASR)
- Reduced permeability and shrinkage
- Reduced potential for efflorescence

At present, most DOTs refer to the chemical requirements of AASHTO M321 for metakaolin for its use in hydraulic cement. The Illinois DOT provides a special provision which includes alkali-silica reaction mitigation requirements where the average alkali content (Na₂O + 0.658K₂O) of high reactivity metakaolin must be less than 1.0%. In addition, the content of silicon dioxide (SiO₂), aluminum oxide (Al₂O₃), and iron oxide (Fe₂O₃) must exceed 80%. The Texas DOT provides an 85% requirement for the same chemical composition [8]. For sulfate resistance, the Colorado DOT requires that high-reactivity pozzolan mixtures have less than 0.10% expansion at 18 months when tested according to ASTM C 1012, whereas Class 2 concrete requires less than 0.05% expansion at 6 months

The Minnesota DOT limits metakaolin to 10% of Portland cement by weight, whereas fly ash and ground granulated blast-furnace slag is limited to 20% of Portland cement by weight. The Missouri DOT approves a maximum of 15% replacement of Portland cement on a pound for pound basis in all concrete. The California DOT recommends metakaolin use in dosages ranging from 5% to 10% by mass of the cementitious material, while the Montana DOT allows up to 20% by weight of the total cementitious material. Ramezanianpour & Jovein [9] recommended that the optimum replacement of metakaolin be 12.5% and 10% at water-to-cement ratio of 0.4 and 0.35, respectively. In Nebraska, the maximum pozzolanic content should not exceed 15%–25% of the total cementitious material. Wisconsin requires that metakaolin be acquired from an approved supplier on the department's approved product list. Furthermore, the supplier must have a quality management program in place, where daily testing is performed to determine uniformity.

Current GDOT specification for mass concrete (special provision to the Section 500) includes the maximum allowable internal temperature of 158 °F and temperature differential of 35 °F between interior and exterior portions of the designated mass concrete element. The special provision also states that slag may comprise no more than 75% by mass of total cementitious and pozzolanic materials. Class F fly ash may comprise no more than 40% by mass of total cementitious and pozzolanic materials. When a combination of multiple different pozzolans is used, the total amount may be no more than 75% by mass of total cementitious and pozzolanic materials.

With a shortage of fly ash and slag in the state, it is possible to consider supplementary cementitious materials such as metakaolin to control heat of hydration; however, prior studies report conflicting conclusions on the effect of metakaolin (i.e., microsilica) on the heat of hydration. In some research the replacement of cement by 10% and 20% microsilica slightly reduced early heat of hydration [10], but this was not the case in other studies [11, 12]. At the same time, the physical characteristics and chemical composition of metakaolin play an important factor in determining the effect on heat of hydration. Alshamsi [12] limited cement replacement to 10%, and the chemical composition of metakaolin differs from what is available in today's market. Therefore, it is necessary to evaluate the feasibility of using metakaolin products available in the Georgia market to reduce the heat of hydration in mass concrete elements. In a recent study [13], increased metakaolin replacement (from 10% to 14%) minimized the total heat evolved, although 10% was found optimal with the consideration of mechanical properties.

An extensive survey of state DOTs' specifications and other available resources is necessary to fully understand current practices and challenges in relation to the usage of metakaolin and other supplementary materials as partial replacements for cement. Furthermore, it is important to determine whether and how metakaolin should be specified.

1.2 Problem Statement

There is a tangible risk of the coal market failing to sustain the current volume of fly ash in U.S. concretes. As a result, alternative supplementary cementitious materials need to be evaluated to maintain the market habits of the ready-mix industry. For Georgia, the most obvious and feasible choice is metakaolin. The kaolin industry is prominent in Georgia,

and the use of metakaolin to improve concrete quality is not a new practice. In fact, metakaolin has had a large presence in the literature for over two decades now. Furthermore, several state DOTs have adopted and specified commercial metakaolins for use in concrete. Even though Georgia is a world leader in the production of kaolin products, the use of metakaolin has yet to be specified in GDOT's Standard Specifications.

The U.S. Geological Survey (USGS) estimates that nearly 8.5 million metric tons of kaolin are mined from Georgia each year [14]. Kaolin has many existing applications not limited to the following: ceramics, toothpaste, paint, and cosmetics. According to the Georgia Mining Association, the kaolin industry in Georgia employs over 4,400 Georgians, which amounts to over \$232 million in pay and benefits [15]. This is a large market with room to sustain the ready-mix concrete industry. Lastly, metakaolin is not a byproduct of another process. Fly ash, silica fume, and blast furnace slag are all secondary materials. Unlike these supplementary cementitious materials, metakaolin ensures quality..

Replacing a portion of cement with fly ash creates a cementitious material that when used as an input with aggregates, water, and other compounds produces a concrete mix that is well-suited for road, airport runway, and bridge construction. However, there has been a fly ash shortage in the Mid-Atlantic region which may have an impact on cement concrete producers and thus costs of construction materials for GDOT projects.

Placements of mass concrete demand considerable temperature rise control due to the heat of hydration of cementitious materials. Typical temperature rise in a concrete mixture ranges from 80 °F to 100 °F. ACI recommends the placement temperature of 58 °F below for 100 °F temperature rise concrete; however, it is particularly challenging to meet the temperature requirement in Georgia. Generally, the temperature rise at concrete placements can be reduced to around 70 °F with a large percentage of Portland cement replaced with Class F fly ash or slag. Yet there has been a shortage of fly ash and slag, calling for the replacement of these materials with alternative binder systems to allow reductions in temperature for mass concrete construction (e.g. large columns and foundations for bridges and other transportation structures).

Cement hydration produces a rise in internal temperature, and the outer concrete surface cools faster than the core of the section. By thermal expansion/contraction, the temperature differential induces thermal stress at the surface. Once the maximum

temperature in the interior exceeds the accepted threshold value, delayed ettringite formation (DEF) can occur in mass concrete elements. Therefore, DEF can be prevented by limiting the internal concrete temperature during its very early life. In prior research, the maximum temperature suggested to prevent DEF in concrete elements is 160 °F [16]. An acceptable temperature can be achieved by explicitly specifying the allowable temperature range, limiting cement content, or using low heat supplementary cement materials.

Current GDOT mass concrete provisions do not allow high-early-strength cement, metakaolin, silica fume calcium chloride, and accelerating type admixtures unless an adiabatic temperature study is completed showing temperature rise significantly less than that of plain unmodified concrete. GDOT could benefit by developing mixture parameters using metakaolin with other Georgia-based materials. Currently, GDOT specifications do not allow Class N pozzolan in concrete. With the availability of kaolin in middle Georgia, GDOT can take advantage of this material to improve the overall properties of concrete mixtures and decrease demand for cement and fly ash. Furthermore, GDOT can control the maximum internal temperature and temperature differential in mass concrete elements by incorporating supplementary cementitious materials such as metakaolin.

1.3 Objectives

This research study aims to find natural, lightly processed, and economical alternatives to fly ash that perform similarly to Class F fly ash with regards to pozzolanic reactivity and provide comparable compressive strength, workability, drying shrinkage, thermal expansion properties and resistance to alkali-silica reaction, sulfate attack, and chloride ion penetration. Metakaolin is a naturally-occurring pozzolan and is included as an ASTM C618 Class N Pozzolan. As a pozzolan, metakaolin would provide similar improved concrete performance in the form of increased workability, decreased permeability, improved strength and durability, and reduced shrinkage.

The primary objective of this project is to determine the usefulness of Class N pozzolan in each of GDOT's concrete classes (Classes 1 and 2 for Pavements and AAA, AA1, AA, A, B, and CS for Concrete Structures). The study identifies the appropriate limits of metakaolin to be used in mixtures and the subsequent concrete performance.

1.4 Significance of Research

The primary benefit of this study will be the identification of reasons for adopting Class N Pozzolan as a viable option for inclusion in concrete specifications. This project will provide appropriate supporting information for its acceptance or rejection. If Class N Pozzolan is deemed acceptable, it would provide GDOT with another viable supplementary cementitious material local to Georgia.

2. LITERATURE REVIEW

There has been a rapid development in the application of sustainable materials in concrete design. Modern concrete consists of five basic ingredients: rock, sand, Portland cement, water, and air. By far, the most expensive and environmentally costly material in this system is cement. During the production of cement clinker, CaCO₃ (calcium carbonate) is converted into calcium oxide via calcination inside a rotary kiln [17]. The second product, CO₂ (carbon dioxide), is then emitted or retained. A simplified chemical equation is given as Eq. (1).

$$CaCO_3 + heat \rightarrow CaO + CO_2$$
 (Eq. 1)

The Intergovernmental Panel on Climate Change (IPCC) states that cement production is the largest emitter of CO₂ in the industrial sector [18]. Worldwide, for every ton of cement produced, approximately 0.82 tons of carbon dioxide are released into the atmosphere [19]. The significance is that approximately 5% of the world's anthropogenic carbon emissions can be traced to the production of cement [20]. Because cement production is both financially and environmentally costly, reducing the proportion of cement in concrete mixtures has gained and remained popular for decades.

To this end, supplementary cementitious materials (SCMs) have played a large role in reducing the amount of cement needed to meet required concrete quality. When properly specified, SCMs can benefit a concrete mixture in five ways:

- 1. Reduce costs
- 2. Improve fresh and hardened properties of concrete
- 3. Reduce environmental impact

- 4. Reuse waste materials
- 5. Enhance aesthetics

An SCM is any material that chemically reacts with hydrating cement to produce additional cementitious compounds. These materials are then further categorized based on their chemical reactions; a SCM can react either hydraulically or pozzolanically within the cement paste system. Once activated, a hydraulic material will create additional calcium silicate hydrate (C-S-H) similar to that of the ordinary Portland cement (OPC) hydration reaction by reacting with the water in the mixture. A pozzolan, however, reacts with a product of the cement hydration (calcium hydroxide, or CH) to produce additional cementitious products. While this reaction will be covered in more detail in Section 3.0, a brief chemical description is given as Eq. 2.

$$S + CH + H \rightarrow C - S - H \tag{Eq. 2}$$

According to the Portland Cement Association (PCA), SCMs are used in at least of 60% of all ready mixed concrete [21]. The three most commonly used SCMs are fly ash (FA), blast furnace slag (BFS), and silica fume (SF). As a result, these are historically the SCMs that have been adopted and specified for use by U.S. state departments of transportation (DOTs). In recent years, however, several state DOTs have allowed for the use of a calcined clay called metakaolin (MK).

2.1 Overview

2.1.1 Introduction

Metakaolin (MK) is an aluminous and siliceous natural pozzolan that conforms to ASTM C618 [22] and is the byproduct of thermally or mechanically activating kaolin clay. Typically, kaolin clay that is used in the production of MK contains a high percentage (40%–70%) of the clay mineral kaolinite (Al₂Si₂O₅(OH)₄) [23]. Kaolinite is mined and used in paper, ceramics, toothpaste, cosmetics, paint, and many other products. In its dehydroxylated form, MK can be used in concrete to enhance mechanical properties and increase durability via its participation in the pozzolanic reaction, while also improving the aesthetic appeal with its white color. One of the most recently implemented SCMs [24],

MK differs from most other SCMs in that it is a primary product. This allows for strict quality standards, thereby providing an option for consistent, high-performance concrete.

2.1.2 Manufacturing and Processing

Kaolin is rigidly structured. Before activation, kaolin consists of alternating sheets of tetrahedral silica (SiO₄) and octahedral alumina (AlO₆) that are linked via oxygen atoms. These connecting oxygen atoms are bound via adjacent hydroxyl (OH)⁻ groups, which are broken and evaporate as water during the activation process (Eq. 3) [25]. Kaolin can be thermally or mechanically activated, although thermal activation is far more prevalent [26]. Activation is perfect if all hydroxyl groups binding alumina and silica sheets in the kaolin are broken. This dehydroxylation results in a disorganized, non-crystalline structure that is highly reactive. The amorphous nature of MK is the source of its reactivity.

$$OH + OH = H_2O \uparrow + O$$
 (Eq. 3)

The process of thermally activating kaolin is referred to as calcining and involves heating finely-divided kaolin at high temperatures for an extended period. The temperature and rate of calcination play a large role in determining the reactivity of the MK that is produced. A review performed by Rashad evaluated the various combinations of calcining temperatures and time used in previous research and found that the optimum range of temperatures was in the ballpark of 600–850 °C [27]. The optimum calcining time varied by temperature, though calcining times between 1–12 hours were the most prevalent. These differences could largely be explained by the differences in kaolin composition. Diffo et al. found that the loss on ignition (LOI) and amount of residual kaolinite (unconverted) increase with the rate of calcination [28]. This indicates that a slower rate of calcination is preferable so long as the temperature is appropriate. Ultimately, the calcining method determines the level of reactivity of the finished MK product. Low temperatures will insufficiently dehydroxylate the kaolin, resulting in a low-reactivity MK. Alternatively, excessively high temperatures will result in the recrystallization and conversion of MK to inert ceramic materials, such as silica (SiO₂), spinel (2Al₂O₃·3SiO₂), and mullite

(2[3Al₂O₃·2SiO₂]) [23]. A successful activation hits the sweet spot in-between these two extremes.

Fitos et al. [26] demonstrated that mechanically activated MK can be competitive to MK that has been produced via thermal activation. More interestingly, several kaolins were used in the study, and some responded better to thermal activation and others to mechanical. Again, this is most likely due to the physical and chemical differences among the kaolins. These properties will be discussed further in Section 2.2.3.

2.1.3 Physical and Chemical Characteristics

The general formula for MK is Al₂O₃·2[SiO₂,] and is typically characterized in the literature by two properties: material fineness and composition by oxides.

MK is generally white and exhibits a high GE brightness, making it useful in architectural applications. For example, as will be discussed later, MK concrete generally sees high early-strengths which make it ideal for prestressing applications. The most common SCM used for this purpose is silica fume (SF), and MK has shown itself to be comparable to SF in ability to achieve high early-strength in concrete. The difference between the two is aesthetic, as SF tends to make the concrete darker with its gray color. MK is also typically a very fine material, falling somewhere between cement and SF (surface area $\approx 15 \text{ m}^2/\text{g}$) [24]. The level of material fineness affects the rate and magnitude of reaction once inside the concrete mixture.

As previously mentioned, MK is predominantly an aluminous and siliceous material. However, it also contains other oxides. MKs with low percentages of these oxides (excluding Fe₂O₃) tend to imply a higher purity MK. Silica (or silicon dioxide) constitutes the largest portion of MK, typically on the order of 50%–55% of the MK by mass. Close behind is alumina (or aluminum oxide) which tends to make-up 40%–45% of the MK by mass [29]. Both alumina and silica contribute to the enhancement of the concrete matrix via the pozzolanic reaction. This will be discussed in more detail in Section 3.1.4. Generally, MKs with a Al₂O₃ + SiO₂ + Fe₂O₃ greater than or equal to 90% are referred to as high-reactivity MK (HRM). This notation will not be used in this paper. MKs of all

oxide makeups will be referred to solely as MK. A summary of the physical and chemical properties of MK can be seen in Figure 1.

Particulars ^a	(Dry, Calcined)	N Pozzolan
Physical characteristics		
Specific gravity	2.5-2.6	_
Bulk density (ton/m³)	0.3-0.4	_
Color	Off-white	
TAPPI (GE) brightness	79-86	
Fineness, retained on 325 mesh (45μm) sieve (max %)	<0.1-0.2	34 (1, wet sieving)
Fineness, average particle size (μm)	1.0-9.5	_
Specific surface, nitrogen adsorption (m ² /g)	9.5-18	_
Pozzolanic activity index—cement (min %)		
7 day	_	75 (85)
28 days	_	75
Increase of drying shrinkage of mortar bars at 28 days (max %)	-	(0.03)
Chemical composition (% mass)		
Silicon dioxide (SiO ₂)	46.6-58.1	_
Aluminum oxide (Al ₂ O ₃)	35.1-45.3	
Iron oxide (Fe ₂ O ₃)	0.38 - 4.64	
Oxides of silicon, aluminum, iron $(SiO_2 + Al_2O_3 + Fe_2O_3, min \%)$	>82.08	70 (85)
Calcium oxide (CaO)	0.02 - 2.71	
Magnesium oxide (MgO)	0.03-1.02	
Potassium oxide (K ₂ O)	0.1 - 3.17	
Sodium oxide (Na ₂ O)	< 0.01-0.4	
Available alkalis as Na2O, (max %)b	0.08-2.49	1.5(1)
Titanium oxide (TiO ₂)	0.01-2.27	
Sulfur trioxide (SO ₃ , max %)	0.07-0.99	4.0
Moisture content (max %)		3.0
Loss on ignition (max %)	0.51 - 2.52	10.0 (3)

Figure 1 – Physical and chemical properties of metakaolin [24].

2.1.4 The Pozzolanic Reaction

The consensus within the literature is that MK contributes to concrete performance in three ways [24]. The first is the filler effect. As with SF, the fineness of MK densifies the paste matrix. The second is the acceleration of the cement hydration. These two contributions

will be discussed when appropriate in the subsequent sections. The last and most influential will be discussed in this section: the role of MK in the pozzolanic reaction.

The pozzolanic reaction occurs when a finely-divided siliceous (or siliceous and aluminous) material reacts with calcium hydroxide (Ca(OH)₂) in the presence of water to produce additional calcium silicate hydrates (C-S-H), calcium aluminate hydrates (C-A-H), or calcium aluminosilicate hydrates (C-A-S-H). CH is a primary product of the cement hydration reaction and is the fuel for the pozzolanic reaction. While the CH helps to maintain the pH necessary to produce stable hydrate phases, it contributes little strength to the concrete matrix and is prone to leaching [21]. Conversely, C-S-H is the most dominant strength-giving product of the cement hydration reaction, and the C-S-H produced during the pozzolanic reaction is similar in composition [30]. However, because MK also contains high amounts of alumina, C-A-H and C-A-S-H products are produced during its pozzolanic reaction, as well. MK consistently ranks higher on the pozzolanic activity index because of its alumina content [13]. The abbreviations for the various hydrate phases are used for convenience as well as to indicate that the products are stoichiometrically variable. Common MK hydration products are C₂ASH₈ (stratlingite), C₄AH₁₃, and C₃AH₆ (hydrogarnet).

In short, the pozzolanic activity of MK strengthens the concrete matrix by introducing additional structural hydrates and partially consuming the CH produced by cement hydration.

2.2 Application

2.2.1 Specifications for Metakaolin's Use in Other States

Although the Georgia Department of Transportation (GDOT) has not yet prescribed the use of MK in their concretes, the benefits of MK are reflected in their presence in other state DOT specifications. It is worthy to note that several parameters seem to be common among most DOT specifications. All states reference American Association of State Highway and Transportation Officials (AASHTO) and/or American Standards for Testing and Materials (ASTM) standards, and universally require that the MK product used be on

an approved supplier list of some kind (analogous to QPL for GDOT). However, some states provide additional requirements. The requirements outlined here are current to 2008.

Florida

- MK conforms to ASTM C618 [22]
- has an Al₂O₃ + SiO₂ + Fe₂O₃ content greater than or equal to 85%
- has a LOI less than or equal to 3% by mass
- pass greater than 99% MK through a #325 sieve
- display greater than 85% strength activity index at 7 days as per ASTM C311 [31]
- be comparable to a SF concrete mixture
- display acceptable strength and durability parameters as per ASTM standards:
 - o C39 (compressive strength) [32]
 - o C157 (unrestrained shrinkage) [33]
 - o C1012 (sulfate resistance) [34]
 - o C1202 (chloride ion penetrability) [35]

Illinois

• MK conforms to AASHTO M321 [36]

Montana

- MK conforms to AASHTO M295 [37]
- MK can replace a maximum of 20% cement

Nebraska

- MK conforms to ASTM C618 [22]
- MK replaces 15%–25% of cement
- MK content does not exceed 27% when using Type IP cement

Nevada

- Conforms to ASTM C618 [22]
- MK has a LOI less than or equal to 5%
- MK does not exceed 20% replacement of cement
- If Type IP cement is used, the alkali content cannot exceed 0.60% unless less than 0.05% expansion is observed at 6 months as per ASTM C227 [38]

New York

- Must be treated just as SF
- Silica content must be \pm 7% from acceptable contents in ASTM C618 [22]
- Contains chloride content less than or equal to 0.20% as per AASHTO T260 [39]
- MK contains a maximum of 5% material retained on #325 sieve

Oregon

- MK meets AASHTO classification outlined in M295 [37]
- MK has LOI less than or equal to 1.5%
- MK has moisture content less than or equal to 1%
- MK contains a maximum of 30% material retained on #325 sieve

Pennsylvania

- MK meets standards outlined in AASHTO M295 [37]
- MK has a LOI less than or equal to 6%
- If reactive aggregate is used, alkali contents in cement must be less than or equal to 1.5%
- Concrete must reduce expansion as per ASTM C411 by at least 50% [40]
- If MK is being used to mitigate ASR, a 15%–25% replacement must be used

Texas

- Must conform to ASTM C618 [22]
- $Al_2O_3 + SiO_2 + Fe_2O_3$ greater than or equal to 85%
- Alkali in cement must be less than or equal to 1%
- MK LOI must be less than 3%
- Less than 1% MK retained on 45 mm sieve
- Concrete must be 85% of strength activity index at 7 days when compared to the control
- Must have less than 3% increase in mortar bar shrinkage at 28 days
- Density of the last 10 concrete samples must not deviate more than 5%

Utah

• MK must conform to ASTM C618 [22]

Wisconsin

• MK must conform to ASTM C618 [22]

2.2.2 Applicable GDOT Specifications

This section serves to summarize the GDOT specifications that will be directly relevant to the present study. For the sake of brevity, the sections which are indirectly affected (e.g., pavement thickness, construction requirements, etc.) by the addition of MK will not be included in this report.

2.2.2.1 Traditional Concrete Materials

Neglecting chemical admixtures, concrete mixtures that adhere to the GDOT requirements necessarily contain course aggregate (rock), fine aggregate (sand), cement, water, and air.

Course aggregate must be crushed stone, gravel, or an acceptable synthetic aggregate. Synthetic aggregates include expanded clay or shale. It is not permitted to use an aggregate that displays greater than a 15% weight loss upon soundness testing. Furthermore, the aggregate gradation must conform to the standard sizes given in Table 1. It should be noted here that most of these standard sizes are not permitted for GDOT pavement or structural applications. This issue will be discussed in Sections 3.2.2.3 and 3.2.2.4 of this report.

Non-inert aggregates can cause extensive damage to fresh and hardened concrete mixtures. Therefore, Subsection 800.2.01.A "Course Aggregates" provides restrictions on the composition of rock used. It is forbidden to use any aggregate that is widely known to cause deleterious reactions. Furthermore, aggregates that contain chrysotile are not permitted for use as unbound surfacing for roads or as a soil-stabilizing subgrade. In addition, the GDOT has specified that the following limitations be observed: micha schist (as defined by ASTM C 294 [41]) content shall be no greater than 5%, less than 1.5% of aggregate may pass through the No. 200 (75 µm) sieve, elongated aggregates with a length more than five times the average thickness shall not exceed 10%, and sulfur content is limited to 0.01%.

Sand is generally less prone to reactivity and therefore GDOT Section 801 is much smaller than Section 800 (Course Aggregate). Allowed sands for concrete and mortar

mixtures are natural sands, manufactured sands, or a blend of natural and manufactured sands. Manufactured sands derived from course aggregate will demonstrate reactivity (or non-reactivity) in the same manner as the source material; therefore, the composition of the source course aggregate should be investigated. Analysis should be done on manufactured sand, as well. Clay lumps, coal, and lignite are each restricted to 0.5% of the total. All other detrimental substances may combine to form no more than 2.0% of the total. A petrographic (ASTM C 295 [42]) analysis conducted on the material retained on the No. 16 sieve must be used to determine these percentages.

Table 1 – Standard sizes for course aggregate (GDOT, 2013).

SIZE	SI SQU	IINAL ZE JARE NINGS	АМС	DUNTS	FINER THA	N EAC	H LABO	RATOR WEIGH		E (SQUA	RE OPENII	NGS). %	, BY
	(1)	mm	2 ½"	2"	1 1/2"	1"	3/4"	1/2"	3/8"	No. 4	No. 8	No- 16	No. 50
			63 mm	50 mm	37.5mm	25 mm	19 mm	12.5 mm	9.5 mm	4.75 mm	2.36mm	1.18 mm	300 µm
3	2-1	50 - 25	100	90- 100	35-70	00- 15		00-5					
357	2-No. 4	50 - 4.75	100	95- 100		35- 70		10- 30		00-5			
4	1 ½ - 3/4	37.5 - 19		100	90-100	20- 55	00- 15		00-5				
467	1 ½- No. 4	37.5 - 4.75		100	95-100		35- 70		10- 30	00-5			
5	1-1/2	25 – 12.5			100	90- 100	20- 55	00- 10	00-5				
56	1-3/8	25 – 9.5	W21222		100	90- 100	40- 75	15- 35	00- 15	00-5		12226	
57	1-No. 4	25 – 4.75			100	95- 100	1000000	25- 60		00- 10	00-5		
6	³/ ₄ -3/8	19 – 9.5				100	90- 100	20- 55	00- 15	00-5		-571776	
67	%-No. 4	19 – 4.75	(1 20022)			100	90- 100		20- 55	00- 10	00-5	577174X	
68	%-No. 8	19 – 2.36	A-11-1-1	3 -111-1		100	90- 100	55000	30- 65	05- 25	00-10	0-5	
7	½-No. 4	12.5 – 4.75					100	90- 100	40- 70	00- 15	00-5		
78	½-No. 8	12.5 – 2.36	8 8888		(1001)		100	90- 100	40- 75	05- 25	00-10	0-5	
8	3/8- No. 8	9.5 – 2.36						100	85- 100	10- 40	0-10	0-5	
89	3/8- No. 16	9.5 – 1.18						100	90- 100	20- 55	0-15	0-10	0-5
9	No. 4- No. 16	4.75 – 1.18							100	85- 100	10-40	0-10	0-5

Standard sizes for the fine aggregates are fewer and are provided in Table 2.

Table 2 – Standard sizes for fine aggregate (GDOT, 2013).

Size	Description	То	tal Percer	nt by Wei	ght Passin	g Each Sie	ve
No.		3/ 8 in (9.5 mm)	No. 4 (4.75 mm)	No. 16 (1.18 mm)	No. 50 (300 μm)	No. 100 (150 μm)	No. 200 (75 μm)
10 NS	Natural concrete sand	100	95-100	45-95	8-30	1-10	0-3
20 NS	Natural mortar sand	100	100	90-100	15-50	0-15	0-5
10 SM	Standard manufactured concrete sand	100	95-100	45-95	8-30	1-10	0-4
10 FM	Fine manufactured concrete sand	100	95-100	45-95	15-42	6-22	0-9

As with the coarse aggregate, not all fine aggregate sizes are permitted for use in concrete pavements and structures. This is discussed in Section 3.2.

All Portland cements (Types I, II, III, IV, and V) that adhere to the low alkali and false set requirements of AASHTO M 85 are permitted for use in GDOT concrete, given that their intended use does not violate any other GDOT specifications.

A good rule-of-thumb holds that if water is potable, its use is permitted in concrete mixing. GDOT Subsection 880.2.01 dictates that "drinking water that is used for ordinary household use" is acceptable for mixing without further testing. Formally, however, there are many stipulations on water content. For instance, the alkalinity as calculated in terms of calcium carbonate, total organic solids, total inorganic solids, and sulfate (SO₄) contents may be no greater than 0.05%. In addition, the chloride content may be no greater than 0.01%.

2.2.2.2 Admixtures (GDOT Section 831)

Optional and permissible additions to the materials outlined in Section 3.2.2.1 are certain SCMs (fly ash and GGBS) and chemical admixtures (for this study HRWRAs and AEAs).

Admixtures that are not on the GDOT Qualified Products Lists (QPLs) are not permitted for use in GDOT concretes. Relevant QPLs are QPL-13 ("Air-Entraining Admixtures"), QPL-14 ("Chemical Admixtures for Concrete"), and QPL-30 ("Fly Ash and Slag Suppliers").

As the air content of a concrete mixture increases, the available strength generally decreases. Thus, the addition of an AEA requires compressive and flexural strength tests

at 7 and 28 days. These strength tests will be in accordance with the testing requirements outlined in Sections 3.2.2.3 and 3.2.2.4. In addition, the use of an AEA is conditional upon the fact that it is pursuant with AASHTO M 154 and that the desired AEA appears in QPL-13.

Other permissible chemical admixtures are present in QPL-14. They must also meet the physical, uniformity, and equivalence requirements outlined in AASHTO M 194 for Types A, B, C, D, E, F, or G unless otherwise specified. Here, length changes can be ignored. The admixtures are not permitted to contain more than 0.80% chloride, calculated as calcium chloride. In addition, no air-entrainment may be used if the air content in a standard mixture (without AEA) exceeds 4.0%.

SCMs that are outlined in GDOT Standard Specifications include fly ash, raw or calcined natural pozzolans, GGBS, and microsilica (silica fume). With the exception of microsilica, all approved mineral admixture products are contained in QPL-30. Fly ash (Classes C and F) and Class N pozzolans shall meet the requirements in AASHTO M 295. Any GGBS used shall conform to AASHTO M 302, and microsilica shall conform to AASHTO M 307. While GDOT Standard Specifications currently allow the use of raw or calcined pozzolans that meet the requirements of AASHTO M 302, they are still not permitted if they do not appear on any QPL. The applicable QPL-30 does not yet contain any MK products (MK is a Class N pozzolan). In addition, unlike fly ash and GGBS, no maximum allowed percentage is specified for concrete pavements or structures. The current presence of MK in GDOT's specifications is therefore superficial, as its use is not yet permitted.

2.2.2.3 Portland Cement Concrete Pavement (GDOT Section 430)

While the use of MK as a mineral admixture in GDOT Class I and II pavements is not yet allowed, the use of fly ash and blast furnace slag (GGBS) is allowed given that the mixture design does not exceed the allowable percentage replacement for each, that Type IP cement is not used, and the mineral admixture meets the requirements of GDOT Subsection 430.3.06, "Quality Acceptance." For fly ash, the maximum percentage of replacement allowed by mass is 15%. Blast furnace slag is allowed to replace up to 50% of the cement content given that the National Weather Service predicts a five-day forecast of

temperatures exceeding 60 °F (15 °C). If projected temperatures are less, the percentage replacement by GGBS is restricted to 30%.

For Portland cement concrete pavements, only coarse aggregate size Nos. 467, 67, or 57 are permitted. Likewise, only fine aggregate size No. 10 is permitted.

Subsection 430.3.06 dictates that for a GDOT Class I pavement a minimum cement content of 541 lb/cy (320 kg/m³) is required as well as a maximum w/cm of 0.53. Similarly, for a GDOT Class II pavement a minimum cement content of 564 lb/cy (335 kg/m³) is required in addition to a maximum w/cm of 0.50. For both mixtures, the desired air content range is 4.0%–5.5%, with 3.0% the minimum allowed and 6.5% the maximum.

All mixture designs must also meet compressive and flexure strength requirements in order to further validate the mixture design. Compressive tests are to be done in accordance with AASHTO T 126 and T 22. Flexure tests are to be done in accordance with AASHTO T 126 and T 97. A Class I mixture meets compressive strength requirements if all test specimens (a minimum of six) fail above the Job Performance Value (JPV). The JPV for a GDOT Class I pavement is 3,000 psi + 0.18R (20 MPa + 0.18R), where R (range) is the difference in the largest and smallest observed value. Similarly, the JPV for a Class II pavement is 3,500 psi + 0.21R (25 MPa + 0.21R). Both must exceed JPVs with cylinders broken at 28 days. Design Acceptance Requirement (DAR) is specified for flexure strength testing, where a minimum of nine cured specimens must be made, and three specimens are taken from each of three trial batches. As with the compressive tests, these specimens must be tested for 28-day strengths. GDOT Class I pavements must meet a minimum DAR of 600 psi + 0.67s (4.1 MPa + 0.67s), where 's' is the standard deviation of all specimen flexure strengths. A standard deviation greater than 37 psi (255 kPa) is not permitted.

2.2.2.4 Concrete Structures (GDOT Section 500)

Concrete pavements are organized into three classes: Class I, Class II, and Class HES (which was not discussed above). Concrete structures, however, are subdivided into six classes: AAA, AA1, AA, A, B, and CS. The required compressive strength and minimum cement content decrease in this order, such that AAA is the strongest class and CS is the weakest. It follows then that w/cm increases in this order. Table 3 provides acceptable values of each metric.

Table 3 – Various requirements for structural concrete classes (GDOT, 2013).

				Englis	h			
Class of Concrete	(2) Coarse Aggregate Size No.	(1 & 6) Minimum Cement Factor Ibs/yd ³	Max Water/ Cement ratio lbs/lb	accepta	Slump nce Limits (in) er-Upper	(3 & 7) Entr Acceptance (% Lower-	ce Limits	Minimum Compressive Strength at 28 days (psi)
"AAA"	67,68	675	.440	2	4	2.5	6.0	5000
"AA1"	67,68	675	.440	2	4	2.5	6.0	4500
"AA"	56,57,67	635	.445	2	4	3.5	7.0	3500
"A"	56,57,67	611	.490	2	4	2.5 (3)	6.0	3000
"B"	56,57,67	470	.660	2	4	0.0	6.0	2200
"CS"	56,57,67	280	1.400	-	31/2	3.0	7.0	1000 (4)
	Graded Agg.*							8.503
				metric				
Class of Concrete	(2) Coarse Aggregate Size No.	(1 & 6) Mini mum Cement Factor kg/m ³	Max Water/ Cement ratio kg/kg	accepta (r	Slump nce Limits mm)	(3 & 7) Entr Acceptance	Limits (%)	Minimum Compressive Strength at 28 days (MPa)
"AAA"	67.68	400	.440	50	100	Lower-	6.0	35
"AA1"	67,68	400	.440	50	100	2.5	6.0	30
"AA"	56,57,67	375	.445	50	100	3.5	7.0	25
"A"	56,57,67	360	.490	50	100	2.5 (3)	6.0	20
"B"	56,57,67	280	660	50	100	0.0	6.0	15
"CS"	56.57.67	165	1.400	00	90	3.0	7.0	7 (4)
	Graded Agg.	100	1.400					. (-)

At least eight compressive specimens must be made and cured according to AASHTO T 126, where an equal number of specimens is made from each batch. The minimum allowable compressive strength for any of the specimens taken will be the minimum compressive strengths found in Table 3 with the addition of 2.0s, with s being the standard deviation of all test specimens. The standard deviation values are again held to maximums, and these can be found in Table 4.

Table 4 – Standard deviations for classes of structural concrete (GDOT, 2013).

	Standard D	eviation (s)	
Class of Concrete	Psi	(MPa)	
В	370	(2.5)	
А	650	(4.5)	
AA	620	(4.3)	
AA1	540	(3.7)	
AAA	500	(3.4)	

As with concrete pavements, fly ash may supplement cement content in structures up to a maximum of 15% by weight, and GGBS may supplement up to 50% if high early strengths are not needed. Neither may be used in combination with Type IP cement. Again, all SCMs must conform to their respective GDOT subsections (831.2.03.A for fly ash and 831.2.02 or 831.2.03.A.3 for GGBS) which have been covered in more detail in Section 3.2.2.2 of this report.

Moreover, HRWRAs are permitted for use in all five classes of concrete given that the slump is within the limits shown in Table 3 and that the admixture conforms to the GDOT specifications outlined in Section 3.2.2.2 of this report. Likewise, AEAs are permitted as outlined in 3.2.2.2. If an AEA is not necessary or desired for a concrete mixture, the limits for the percentage of entrained air in Table 3 can be ignored.

2.2.3 Availability of Metakaolin in Georgia

Georgia is a global leader in kaolin mining and produces over 5.4 million tons per year [14]. The Georgia Mining Association (GMA) estimates that the economic impact of the kaolin industry on Georgia exceeds \$771 million each year. Moreover, it is estimated that Georgia's kaolin producers generate nearly \$120 million in state, local, and federal taxes. Over 4,400 Georgians are employed by either the mining or processing industries for kaolin, making kaolin the most impactful mineral industry in Georgia [15]. The primary deposits in Georgia lie between Macon and Augusta. Rich deposits also exist along the portion of the Atlantic Seaboard Fall Line that extends into South Carolina. This fall line that runs

through Georgia and into South Carolina is also called the Kaolin Belt. Figures 2 and 3 give context for the location of kaolin mining in Georgia.



Figure 2 – Georgia's portion of the Kaolin Belt [15].

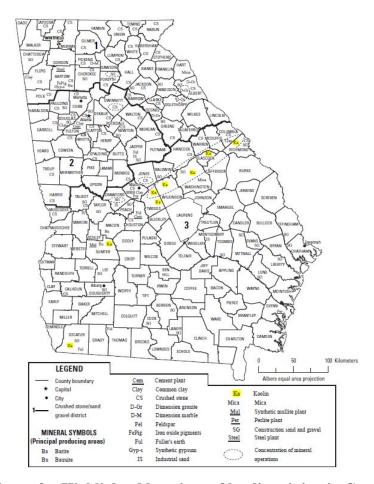


Figure 3 – Highlighted locations of kaolin mining in Georgia [14].

Market research conducted in 2016 by QYResearch identified the top 12 producers of MK in the United States based on factors such as revenue and market presence [43]. The list is as follows:

- BASF
- Daleco Resources
- Imerys
- I-Minerals
- KaMin
- LB Minerals
- SCR-Sibelco
- Thiele Kaolin
- Poraver
- Calix
- Infine Chemicals Co., Ltd.
- Kay Manufacturing Company

2.3 Properties of Concrete Mixtures Containing Metakaolin

The factors that affect the properties of a concrete mixture are numerous, and the inclusion of MK into a mixture brings additional variables. This paper's intent is to inform the day-to-day use of MK. The author proposes that the properties discussed in Sections 2.3.1–2.3.4 will be sufficient to meet this objective. Supplementary information, such as changes in microstructure and concrete chemistry, are contained in Section 2.3.5.

2.3.1 Fresh Properties

2.3.1.1 Workability

In many cases, a high range water reducing admixture (HRWRA) is necessary to maintain workability in a concrete mixture containing fine pozzolans. HRWRAs can be used to decrease the water content of a mixture while maintaining workability, or likewise increase workability without adding additional water to a mixture. The addition of pozzolans (especially highly reactive pozzolans) can significantly increase the water demand in a concrete mixture because additional water is needed for the pozzolanic reaction. Furthermore, with fine SCMs water adsorption pulls available water, and the result is a deficit of water during mixing. With an increase in water demand, a fresh concrete mixture is now less workable. The proper use of a HRWRA can result in the deflocculation of the MK particles, which increases the performance and ease of use associated with the concrete mixture [44].

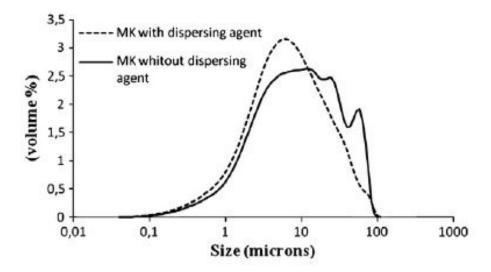


Figure 4 – Particle size distribution of metakaolin [18].

A study conducted by Paiva et al. in 2012 used varying levels of HRWRA to maintain the approximate slump of 3.54 ± 0.39 inches (9 ± 1 cm) [44]. Without a HRWRA, a water to cementitious materials ratio (w/cm) of 0.60, 0.65, 0.70, and 0.75 were required to meet the slump criteria for the control, 10%, 20%, and 30% MK replacements, respectively. As previously mentioned, the addition of a HRWRA can allow for a reduction in w/cm and therefore minimizes the reduction in strength that would normally accompany a greater w/cm. The 10% MK replacement achieved a comparable slump to the control with a w/cm of 0.60 and a HRWRA dosage of 0.08% by weight of total weight of solids. Similarly, the 20% and 30% MK replacements achieved a comparable slump with a w/cm of 0.60 and a HRWRA dosage of 0.15% and 0.20% by weight, respectively.

Paiva et al. studied the effect of a HRWRA on the dispersion properties of concrete mixtures containing 0%, 10%, 20%, and 30% MK [44]. The rheological parameters g and h (yield stress and viscosity, respectively) were studied in order to quantify the effects of the dispersion on fresh and hardened properties of concrete. In the absence of a HRWRA, agglomerates of MK promoted the adhesion of water and air, thus decreasing both the available water in the mixture and increasing the air content. In addition, these larger agglomerates were less reactive than the individual particles of MK. Small compressive specimens were made, and the researchers found that when a HRWRA was used, the compressive strength increased. In contrast, when the water content was increased to maintain the workability, a slight strength decrease was observed.

Dinakar et al. observed a near-linear relationship between the HRWRA dosage and the percentage replacement of cement by MK. The HRWRA used was a polycaboxylate ether (PCE) based super-plasticizer (SP) [45].

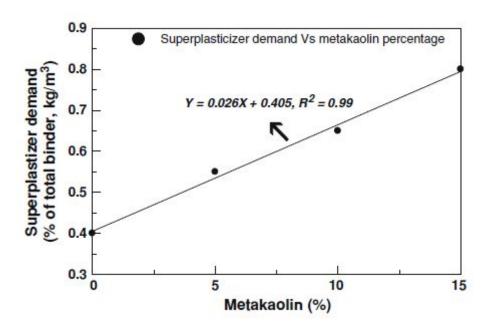


Figure 5 – Plasticizer demand as a function of MK replacement level [45].

Li and Ding investigated the effect of MK on workability and found that MK significantly reduces the workability when compared to control mixtures [46].

The review of available literature by Sabir et al. shows that workability reductions can always be expected when mixing MK concretes [30]. This is due in large part to the material fineness of MK. Notably, in research conducted by Caldarone et al., MK concretes required 25%–35% less HRWRA than their SF counterparts [47]. SF has a higher surface area and material fineness and a slightly lower pozzolanic activity, factors that support an explanation of reduced workability almost exclusively due to material fineness.

2.3.1.2 Setting Time

The literature is undecided on whether MK increases or decreases setting time. In a study performed by Brooks and Johari, researchers found that both the initial setting time and

final setting time were delayed by the inclusion of MK [48]. With the aforementioned 'specific dosage' concept in mind, this research reported initial setting times in increasing order: control, 5% MK, 15% MK, and 10% MK. The setting time for the control was 5 hours, while the setting time for the 10% MK was 6.98 hours. Final setting times followed the same trend, the control at 7.7 hours and the 10% MK at 9.42 hours.

A study by Subasi and Emiroglu was conducted on the effects of a low-reactivity $(SiO_2+Al_2O_3=46.73\%)$ MK on white Portland cement. Here, both the initial and final set times were lengthened by the addition of MK [49]. These effects were most notable at a 30% replacement, where the initial set time was delayed by 15 minutes, and the final set time was delayed by 20 minutes.

Shekarchi et al. observed a systematic decrease in time to initial set when replacing 5%, 10%, and 15% of cement by MK. The greatest difference (102 minutes) was observed between the 10% and 15% MK mixtures [50]. The time to final set varied no more than 36 minutes and was not systematic.

Justice and Kurtis observed that the replacement of cement by 8% MK sharply reduced the time to initial set. This was even further affected by MK material fineness, with the finer MK (surface area equal to 25.4 m²/g) reaching initial set 39 minutes before the coarser MK (11.1 m²/g). The times from initial set to final set were comparable between both MK blended cements and the control case [51].

2.3.2 Mechanical Properties

2.3.2.1 Compressive Strength

Murthy observed that the highest increase in compressive strength occurred when 10% of the OPC was replaced with MK. At 28 day-strength, these cylinders broke at an average of 9.41% higher than the control (100% OPC).

Saravanan found that a 20% cement replacement by MK produced the highest compressive strength when combined with a 10% cement replacement by fly ash. At 28 days, the cylinders for the 20% MK replacement averaged a 29.75% increase in strength from the control [52].

Paiva showed that compressive strength may continue to increase even up to a 30% MK replacement if the agglomerate MK particles are sufficiently dispersed using a HRWRA [44]. When the workability was maintained by increasing w/cm, only the 10%, 20%, and 30% MK mixtures decreased in compressive strength by 2.89%, 9.97%, and 20.47%. When the HRWRA was used to combat the decrease in workability, however, the compressive strengths of the replacement mixtures increased by 4.46%, 17.06%, and 18.37%, respectively. The addition of HRWRA caused the dispersion of MK particles, which facilitated the production of C-S-H while also allowing a lower w/cm. The production of C-S-H and lower w/cm are known to contribute to higher strengths in concrete.

Poon et al. observed that a rapid strength gain between casting and seven days can be observed with MK [29]. The compressive strength gain was also measured in silica fume concrete specimens, and the study showed that the rate of strength gains for MK concretes exceeded even the silica fume concretes. This trend was especially visible at the age of

three days. The researchers attributed this finding to the acceleration of cement hydration as well as the high pozzolanic activity of the MK.

Khatib and Hibbert observed the compressive strength of 10% and 20% replacements of cement by MK and found that the 20% mixture performed the best [53]. The optimum replacement, therefore, varies based on the mixture proportions. Here it is seen that the optimum MK percentage is higher. This could be attributed to several things, but the most likely cause is a relatively high w/cm ratio (0.50). Another contributing factor is that the SiO₂+Al₂O₃ contents of the MK were lower than other studies (here equal to 93.1%). The researchers found that the rate of strength gain was significantly higher in MK concretes up to 14 days of curing and then diminished. Strengths at all ages, however, were higher than the control.

Dinakar et al. observed a maximum compressive strength at a 10% MK replacement with SiO₂+Al₂O₃ contents equal to 92.6% and a w/cm ratio of 0.30 [45].

Subasi and Emiroglu tested the compressive strength of mortars (w/cm = 0.50) with 0%-30% replacement by MK and found that the strength decreased as the replacement level increased [49]. This result is most likely due to the low pozzolanic activity of their MK (SiO₂+Al₂O₃ = 46.73%). Notably, the 5% MK mortar was the only replacement to meet their 52.5 MPa minimum at 90 days of curing.

A review of literature by Sabir et al. reported that generally there is little benefit beyond a 15% MK replacement level for compressive strength [30]. Furthermore, the compressive strengths of pastes and concrete samples alike containing MK are generally higher than those for control mixtures. The effect on compressive strength is most apparent at ages less than 14 days, as the pozzolanic reaction is most active during this time.

Barbhuiya et al. investigated the addition of MK (0%, 5%, 10%, and 15%) on concretes of 0.50 and 0.60 w/cm ratios [54]. Strengths were found to systematically increase with the addition of MK up to 15%. Interestingly, all concretes at 0.50 w/cm displayed higher compressive strengths than those at 0.60 w/cm. Even the w/cm = 0.50 control performed better than the 0.60 w/cm with 15% MK.

Yazici et al. studied the effect of MK content as a partial replacement of cement (0%, 5%, 10%, 15%, and 20%) on the compressive strength of mortars up to 180 days of curing and a w/cm ratio of 0.50 [55]. The MK that was used had a combined Al₂O₃+SiO₂ content equal to 95.89%, for which a significant portion (63.53%) was SiO₂. Blaine specific surface area was 1,177 m²/kg. Results indicated that mortars containing MK achieve compressive strengths greater than the control at all ages other than one day. Only the 5% MK mortar's 1-day compressive strength was greater than the control. The magnitude of compressive strength increase over control varied between 4% and 14%. In addition, Yazici et al. observed the change in compressive strength with elevating temperatures (20 °C, 200 °C, 500 °C, and 700 °C) at the age of 28 days of curing. As the temperature increased, the MK mortars lost their advantage over the control mortar by exhibiting lower compressive strengths. This decrease relative to the control specimens was attributed to the internal stresses induced in the MK specimens. The researchers concluded that the finer pore structure in the MK mortars may have provided for higher vapor pressures when heated and therefore resulted in greater internal stresses than the control. Regardless, the compressive strengths at various temperatures were not significantly less than the control with the exception of the 20% replacement by MK. Additionally, the 15% MK mortar was never out-performed by the control.

Wang et al. studied the effect of MK as a 3%, 6%, and 9% replacement of cement on the compressive strengths of concrete (w/cm = 0.45) [56]. The Al₂O₃+SiO₂ content of the MK was equal to 96.40%. The 9% MK concrete performed the best with a 30% increase in compressive strength over the control at 28 days of curing.

Badogiannis et al. studied the effect of partial cement replacements by MK. Two MKs were used. The first (commercial grade) contained 95% metakaolinite, and the second (MK originating from poor Greek kaolin) contained 49% metakaolinite. The MKs replaced cement by 10% and 20%. Both MKs significantly contributed to strength as early as 2 days of curing, and this trend held at all subsequent ages up to 90 days [57]. At 28 days of curing, the MK originating from Greek kaolin contributed the most strength, and the optimum replacement was found to be by 10% MK. This optimum replacement corresponded to a compressive strength that was 43.2% higher than the control mixture. Interestingly, Badogiannis et al. also produced concrete mixtures that replaced a portion of sand (10% and 20%) with MK. These strengths were higher than both mixtures that replaced cement with MK.

Guneyisi et al. studied the cement substitution of 5% and 15% MK and SF in concretes of 0.25 and 0.35 w/cm ratios. At a w/cm equal to 0.25, the optimum mixtures at 3, 7, and 28 days were 5% MK, 15% MK, and 15% SF, respectively [58]. At a w/cm equal to 0.35, the optimum mixture at all ages was the 15% replacement by MK. While the 15% SF mixture's compressive strength exceeded the 15% MK at 28 days for the w/cm equal to 0.25, the values were of similar magnitude. At a w/cm ratio equal to 0.35, however, the MK blended concrete significantly out-performed the SF blended concrete. Notably, the

MK blended concretes (even at w/cm = 0.25) displayed much higher early-strengths than the SF blended concretes.

Ramezanianpour and Jovein tested concretes with 0% (control), 10%, 12.5%, and 15% MK at w/cm ratios equal to 0.5, 0.4, and 0.35, and at 7, 28, 90, and 180 days of curing [59]. The MK used was highly siliceous (SiO₂ = 74.3%, Al₂O₃ = 17.8%) and had a Blaine specific surface area equal to 3,700 cm²/kg. Typical patterns were observed such as increasing strength with decreasing w/cm ratio. At a w/cm equal to 0.50, the optimum replacements at 7, 28, 90, and 180 days were 10%, 10%, 15%, and 15%, respectively. At a w/cm equal to 0.40, the optimum replacement was 12.5% at all ages. Finally, at a w/cm equal to 0.35, the optimum replacement was 10% at all ages.

Justice and Kurtis observed the effect of varying w/cm ratio and MK material fineness on the compressive strength of concrete [51]. A trend of increasing strength with decreasing w/cm was observed, as is generally expected. The finer MK (25.4 m²/g) achieved higher ultimate strengths as well as displaying a much higher rate of strength gain. The strengths observed in the finer MK at three days were comparable to the strengths observed from using the coarser MK (11.1 m²/g) at seven days of age. The most notable increases in compressive strength from the control were the finer MK at 1 (38.1% greater than the control) and 90 (39.2% greater than the control) days of curing. The only level of replacement used was 8% MK.

Duan et al. demonstrated a correlation between microhardness tests conducted on the interfacial transition zone (ITZ) and compressive strength of concretes containing SCMs [60]. The strengths at all ages can be seen to be greatest for MK, followed by SF, GGBS, and the control, respectively.

Shekarchi et al. reported that concrete with 15% MK replacement of cement saw compressive strength increases of 20% over the control [50].

2.3.2.2 Tensile Strength

Unlike steel, concrete is not an isotropic material, meaning it does not behave mechanically in tension as it does in compression. In applications such as concrete pavements, the tensile loads are carried as an unreinforced concrete beam; thus, it is important that the ultimate tensile load of a mixture is known. Moreover, knowledge of the tensile capacity allows the engineer to understand the size and extent to which cracking will occur. The modulus of rupture (MOR) and the split-cylinder tests (ASTM C78 and C496, respectively) are the two most common tests in determining concrete's ultimate tensile capacity. In both tests, the tensile stresses are found indirectly, as a direct tensile test is difficult to conduct without forming local stress concentrations.

The MOR test was formulated based on a flexural analysis, where the ultimate tensile stress is that which occurs on the bottom face of an unreinforced concrete beam in bending. ASTM C78 dictates a third point bending scheme in which all point loads are equal.

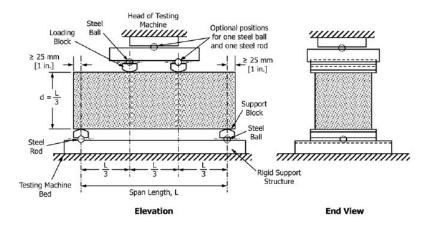


Figure 6 – MOR test setup [61].

It can be shown that the MOR (ultimate tensile stress at the extreme fibers) is given by

$$f_r = \frac{PL}{bd^2}$$

Likewise, an empirical equation for the MOR is specified in ACI 318-14 (Section 19.2.3.1) as

$$f_r=7.5\lambda\sqrt{f'c}$$
 (f'c in psi) or
$$f_r=0.62\lambda\sqrt{f'c}$$
 (f'c in MPa)

The split-cylinder test employs a hoop stress analysis in order to determine the highest tensile stress. When analyzed in this way, the split-cylinder strength is given by:

$$f_t = \frac{2P}{\pi l d}$$

Ultimate tensile stresses calculated from MOR tests tend to produce higher values than their split-cylinder counterparts. In tests conducted by Olanike, split-cylinder strengths of concrete tend to be 60%–80% of the MOR [62].

Dinakar et al. observed an increase in splitting tensile strength with the addition of MK at a w/cm ratio of 0.30. The increase was not systematic with increasing replacement percentages by MK and was found to produce the highest strengths at a 10% replacement [45]. The replacement of 10% resulted in a 5.15% increase in the splitting tensile strength. This optimum replacement percentage is consistent with Dinakar's findings for compressive strength.

Jiang et al. observed that at all curing ages, the flexural capacity of MK mortars were lower than the control at a w/cm ratio of 0.17. However, MK mortars containing steel fibers were stronger than the control fiber mixture in flexure [13]. In addition, the highest flexural strength was seen at a 10% MK replacement level with the inclusion of steel reinforcing fibers. The authors attributed this to the MK enhancing the bond between the steel fibers and the rest of the paste. The inclusion of both MK and fiber reinforcement resulted in an increased flexural toughness (area under load-deflection curve). While MK alone decreases the flexural capacity, the enhanced bond between the fibers and the paste results in an increased pull-out resistance, and thus results in a prolonged ability to resist load under greater deflections.

Flexural tests performed by Subasi and Emiroglu indicated that a low-reactivity MK will decrease flexural strength systematically with replacement level [49]. This decrease is consistent with their compressive strength results. The authors take care to note the larger increase of flexural strength between 28 and 56 days of curing, which they attribute to the pozzolanic action of the MK.

Yazici et al. studied the effect of MK content as a partial replacement of cement (0%, 5%, 10%, 15%, and 20%) on the flexural strength of mortars up to 180 days of curing and at a w/cm ratio of 0.50 [55]. The MK that was used had a combined Al₂O₃+SiO₂ content equal to 95.89%, for which a significant portion (63.53%) was SiO₂. Blaine specific surface area was 1,177 m²/kg. The researchers found that the flexural strength of the mortars containing MK was greater than the control at all ages other than one day. Increases in flexural strength were between 3% and 14% higher than the control at the end of the 180 day curing period. The greatest increase was seen at 15% MK.

Guneyisi et al. observed similar trends to that of the compressive strength when comparing the split-tension strengths of MK and SF blended concretes [58]. The optimum mixtures for a w/cm equal to 0.25 at 3, 7, and 28 days were 5% MK, 15% MK, and 15% SF, respectively. Again, at a w/cm ratio equal to 0.35, the 15% MK blended concrete outperformed both the control and SF concretes at all ages. It is especially noteworthy that the 15% MK at 7 days of curing outperformed the 15% SF at 28 days of curing.

Justice and Kurtis reported that increases in flexural strength observed using MK were in the range of 1–2 MPa [51]. In addition, no clear trend existed between material fineness of the MK and the flexural strength of specimens. At a w/cm ratio equal to 0.40, the 1-day flexural strength attained with the finer MK was equal to the 3-day strength attained with the coarser MK. At higher w/cm ratios, 3-days strengths were observed that were equivalent to 28-day control strengths. As mentioned by Justice and Kurtis, this marked increase in flexural strength from the control has implications for pavements to decrease time until traffic may commence.

2.3.2.3 Modulus of Elasticity

The effect of added MK on the modulus of elasticity (MOE) is dependent upon the percent replacement of cement and on the reactivity of the MK product used. Murthy et al. (using 20 Mircons Limited, Gujarat) replaced OPC with 0%, 7.5%, 10%, 12.5%, 15%, and 17.5% MK and found that the best results were achieved with a 10% replacement, showing a 26.44% increase in the MOE.

Dinakar et al. found that at a w/cm ratio of 0.30, the highest MOE corresponded to a 10% replacement of cement by MK: 47.16 MPa (6840 ksi, a 3.8% increase from the control) [45]. The apparatus used was in accordance with ASTM C 469 [63].

Justice and Kurtis observed an increase in the MOE when using MK as an 8% replacement for cement. The results indicated that the effect of adding MK is more pronounced at lower w/cm ratios and that the material fineness of the MK did not affect the MOE [51]. At a w/cm ratio of 0.40, 0.50, and 0.60, the MOE resulting from the additions of MK increased 18%–19%, 3%–6%, and 8%–11%, respectively.

2.3.3 Creep and Shrinkage Properties

Autogenous shrinkage refers to the volumetric change in a concrete specimen that occurs solely from self-desiccation. This definition excludes all shrinkage resulting from the exchange of water (or other materials) with the outside environment, stresses due to external loads or restraints, and thermal stresses [64]. Typically, the effects of autogenous shrinkage are small in comparison with drying shrinkage; however, in very low w/cm ratios (less than ~ 0.45) autogenous shrinkage can make up a significant portion of the overall shrinkage [21].

Brooks and Johari studied the effects of varying replacement levels of MK (0%, 5%, 10%, and 15%) on both early-age (measured from initial set to 24 hours) and long-term (measured from 1 day to 200 days) autogenous shrinkage of concrete at a water to cementitious materials ratio (w/cm) of 0.28 [48]. With increasing replacement levels of MK, the early-age autogenous shrinkage decreased with the greatest reduction—65%—at 15% MK. This was attributed to the dilution effect, or the reduction of the amount of cement. In addition, HWRA dosages at higher MK contents resulted in a higher 'specific dosage' with respect to the cement contents, and it is therefore possible that the HRWRA was responsible for some retardation of cement hydration before 24 hours. Long-term autogenous shrinkage was higher than the control for all replacement levels but was found

to decrease as the replacement level increased—with 5% MK seeing a 91% increase from the control and 15% MK seeing a 56% increase from the control. Cumulative autogenous shrinkage (the sum of early-age and long-term) was therefore seen to be higher than the control at a 5% MK replacement and lower for the 10% and 15% MK mixtures. Because of the low w/cm, autogenous shrinkage constituted up to 68% of the overall shrinkage observed.

Brooks and Johari also studied the effect of MK replacement levels on drying shrinkage of concrete specimens. Drying shrinkage was calculated as total shrinkage minus autogenous shrinkage. With the inclusion of MK, drying shrinkage was reduced at all replacement levels, and the replacement level had little effect on the magnitude of reduction [48].

At low w/cm ratios, the total shrinkage is reduced as the replacement of MK increases. Also at low w/cm ratios, the lower porosity and finer pore structure that result from the use of MK promote water loss by self-desiccation as opposed to water loss to the environment. Furthermore, it has been proposed that at higher replacement levels by MK, tetracalcium aluminate hydrate (C₄AH₁₃) is replaced by the more voluminous gehlenite hydrate (C₂ASH₈), which in turn reduces the significant autogenous shrinkage that is observed with MK and silica fume concretes [48].

Brooks and Johari were among the first to study the creep response of MK concretes at varying replacement levels in 2001 [48]. In their study, compressive creep was observed at a stress/ultimate strength ratio equal to 0.20, while load-free specimens were made in order to ignore the effect of natural shrinkage strains. The specimens were observed over the course of 200 days. The strain associated with creep was therefore calculated as the

total strain under deformation minus the elastic strain, and minus the aforementioned strain of the load-free specimens. At increasing MK replacement levels, the researchers found both the total and basic creep decreased. This finding is not surprising and is attributed to denser particle packing, the stronger paste matrix, and the stronger paste matrix/aggregate bond that results from the fineness of MK and its pozzolanic action.

Wild et al. [65] studied the shrinkage of MK-OPC pastes and found that both autogenous and chemical shrinkage decreased in pastes containing MK. These effects, seen most predominantly at higher replacements, were attributed to the increased amount of C₂ASH₈ and decreased amount of C₄AH₁₃.

Gleize et al. investigated the effect of MK on the autogenous shrinkage of cement pastes at w/cm ratios of 0.30 and 0.50 [64]. The MK used contained high amounts of Al₂O₃ and SiO₂ (sum = 96%) and constituted replacements of cement equal to 5%, 10%, 15%, and 20%. The three possible causes of autogenous shrinkage were the dilution effect, heterogenous nucleation, and the pozzolanic effect. No expansion was observed at earlyage, and the inclusion of MK decreased long-term autogenous shrinkage. At length scales 0–30 days, autogenous shrinkage of the 0.30 w/cm mixture was higher than the 0.50 mixture. The research also shows that a more dramatic decrease in autogenous shrinkage via inclusion of MK is seen in the higher w/cm mixture. The lowest shrinkage value observed at the end of the trials was the 20% MK mixture at a w/cm equal to 0.50. For the sake of observing autogenous shrinkage without the influence of the dilution effect, the research team molded some specimens (10% and 20% replacement of cement) with inert quartz powder. It was found that a significant reduction in autogenous shrinkage occurs because of the pozzolanic reaction. Samples containing MK displayed more autogenous

shrinkage than the quartz inclusive specimens at early ages but significantly less than the quartz specimens at the end of the 120-day trial. A differential thermal analysis (DTA) seemed to contradict the explanation that the decrease in autogenous shrinkage could be explained by the substitution of tetracalcium aluminate hydrate (C₄AH₁₃) for the less dense gehlenite hydrate (C₂ASH₈).

Guneyisi et al. conducted unrestrained drying shrinkage tests as per ASTM C157. The length measurements were taken every 24 hours for the first 3 weeks and then 3 times per week up to 42 days [58]. The tests indicated that 15% SF was the optimum among 5% SF, 5% MK, 15% SF, and 15% MK blended concretes up until around 24 days of age. It was then surpassed by the 15% MK specimen up to the end of the testing period. At the end of 42 days, the 15% SF and 15% MK blended concretes achieved 42% and 35% less shrinkage than the control specimen, respectively. In addition, restrained ring shrinkage tests were conducted on 5% SF, 5% MK, 15% SF, and 15% MK specimens, where the maximum crack width was measured up to 45 days of age. In descending order, the performance levels of the specimens were 15% SF, 15% MK, 5% SF, 5% MK, and the control [58].

Gleize et al. studied the effect of MK on autogenous shrinkage for cement pastes containing 5%, 10%, 15%, and 20% MK at w/cm ratios of 0.30 and 0.50 [64]. For both water contents, the researchers found that the short-term expansion was comparable to that of the control paste, while the long-term autogenous shrinkage decreased with the use of MK. This study showed that autogenous shrinkage is much higher in the 0.30 w/cm pastes. Results also indicated that the ability of MK to reduce autogenous shrinkage is more efficient at higher w/cm ratios. The use of 20% MK in the 0.50 w/cm paste resulted in a 56% reduction in autogenous shrinkage, while the 0.30 w/cm paste saw a 35% reduction.

The effect of heterogenous nucleation and dilution effect were separated from the effect of the pozzolanic reaction, and it was found that the pozzolanic reaction significantly affects the reduction in long-term autogenous shrinkage.

2.3.4 Durability and Transport Properties

Shekarchi et al. found that a strong correlation exists between many transport parameters. In general, strong correlations exist between measures of concrete durability because the tests are so heavily affected by the pore structure. However, the research team found a poor correlation between resistance to alkali silica reactions and the rest of the durability parameters [50]. Whereas a MK replacement level of 5% was seen to affect the pore structure, its effectiveness was comparable to the control in mitigating ASR. A higher replacement level of 10% was needed to reduce the expansion to less than 0.1%.

2.3.4.1 Chloride Transport

Poon et al. studied the permeability of MK and SF concretes by chloride ions using ASTM C1202 [35]. The tests were conducted on w/cm of 0.30 and 0.50 and measured the cumulative charge in coulombs that were passed through the samples. In this study, the w/cm ratio had a drastic effect on the permeability to chloride ions, with the higher w/cm concrete displaying much higher permeability. Regarding the two SCMs, the MK concretes displayed a higher resistance than the SF concretes, but not drastically. For a w/cm of 0.30, the 10% MK concrete passed the least charge, with 199 Coulombs at 28 days. Alternatively for a w/cm of 0.50, the 20% MK concrete passed the least charge, with 640 Coulombs at 28 days. Both displayed a higher resistance than the control, by far, confirming that SCMs with a high pozzolanic activity and high specific surface area are effective in reducing the

permeability of concrete, thereby greatly influencing transport properties. Interestingly, Poon et al. studied the correlation between the concrete and paste-matrix porosity and the chloride ion permeability. Here, the chloride ion data had a stronger correlation with the concrete porosity, implying that the ion transport depends heavily on both the paste matrix and the paste-aggregate interface.

Dinakar et al. measured the chloride ion permeability of concrete specimens as per ASTM C 1202 [35, 45]. The control specimen passed a total of 1,162 Coulombs in the span of 6 hours, which is classified as a low chloride permeability by ASTM C 1202. In contrast, all specimens including MK indicated a very low permeability. The lowest total charge passed was 148 Coulombs at a 15% MK content.

Tafraoui et al. studied the diffusion and migrations of chloride ions in both MK and SF concretes, with SF concretes well established as effective in mitigating harmful ion transport within concrete. The measured coefficient for diffusion for the MK samples was higher than that of SF concretes [66]. However, the coefficients remained within the same range of one another (10⁻⁴ m²/s). This is on the order of 1,000 times less than that of ordinary concretes and indicates that MK is largely sufficient to limit ion transport. Moreover, these results are especially significant for chloride ion transport because of the relationship between chloride ions and the corrosion of reinforcing steel [66].

Wang et al. studied the effect of MK as a 3%, 6%, and 9% replacement of cement on the bound and unbound chloride concentrations at various depths in concrete specimens (w/cm = 0.45) [56]. The Al₂O₃+SiO₂ content of the MK was equal to 96.40%. The concentrations of the unbound chloride ions in the pore solution were determined via immersing finely ground samples into distilled water and then analyzed using

potentiometric titration. Similarly, the concentration of total chlorides was determined via immersing the ground specimen into an acid solution and performing the titration. The concentration of bound chloride ions was determined by subtracting the total concentration from the free concentration. At a given depth, the research team found the concretes containing MK also contained less free chloride ions and were less permeable than the control. It was also found that while the total chloride content decreased for MK specimens, the bound chloride content increased. RCP tests were conducted, and it was determined that the charge passed could be reduced by 86.4% from the control by replacing 9% of the cement with MK. The chloride binding capacity was also studied with the additional replacement of 5% cement with gypsum (CaSO₄·2H₂O). The results indicated that while the chloride binding capability increases as MK content increases, it decreases when gypsum replaces additional cement. When gypsum is added to the concrete mixtures, the reaction of the C₃A in cement with the sulfate in the gypsum to produce ettringite (AFt phase) is preferred over the reaction of the C₃A with chloride ions to produce Friedel's salt (generally considered an AFm phase).

Badogiannis et al. conducted an in-depth study of the effect of MK on the behavior of chlorides in concrete mixtures. Trials were conducted replacing 10% and 20% of cement and sand with MK [57]. Chloride ingress experiments indicated that specimens containing MK at all depths, save a shallow region near the surface, contain a lower chloride content than the control concrete. In addition, the researchers also measured the chloride binding capacity of a high silica MK and an MK that contained normal amounts. Total chloride ion concentrations (free + bound), as well as free chloride ion concentrations, decreased with successive MK replacements. It was concluded that the alumina content of MK increases

the chloride binding capacity of concrete, and as the binding capacity increases, the chloride diffusion coefficient (measure of chloride diffusion into concrete) decreases.

Corrosion of steel reinforcement inside concrete structures plays a large role in the service life of the structure. Furthermore, the movement of chloride ions inside concrete contribute significantly to the corrosion of steel by removing the passive oxide coating [57]. The corrosion of steel results in voluminous reaction products, which then lead to internal stresses and cracking in the concrete. Concrete specifications for materials are written to limit the intrinsic chloride content; however, extrinsic chlorides still pose a problem.

C₃A reacts with unbound chloride ions in pore solution to produce Friedel's salt. The quantity of Friedel's salt is more closely tied to the Al₂O₃ content than the SiO₂ content [67].

The chloride binding capacity of concrete will determine the extent to which intrinsic chloride ions will stabilize. However, as most chlorides are extrinsic, the resistance to chloride ion transport becomes the most important test parameter.

Ramezanianpour and Jovein observed a drop in total charge passed up to 180 days with a decreasing w/cm ratio. In addition, there was a systematic decrease in total charge passed with increasing replacement levels of cement by MK [59]. Chloride permeability as defined by ASTM C1202 characterized the control, 10%, 12.5%, and 15% MK mixtures as "very low," "very low," "low," and "moderate," respectively. Because the Rapid Chloride Penetration Test (RCPT) is an indirect measurement of resistance to chloride ions, the authors also conducted a salt ponding test in which the diffusion coefficient was calculated [35]. A comparison between the diffusion coefficients and the total charged

passed revealed that the RCPT correlated well with the more direct salt ponding test. A linear best-fit line joining the two returned an R² value equal to 0.9605.

Guneyisi et al. performed accelerated corrosion tests on 0% MK, 5% MK and 15% MK concrete specimens to determine MK's effectiveness in mitigating the corrosion of reinforcing steel inside concrete [68]. The experimental setup entailed concrete cylinders containing steel rebar that were partially submerged in a chloride solution. The steel bars were connected to a power supply that sustained a constant potential of 30 Volts. The indication of failure was the cracking of the concrete specimen. The researchers observed that concrete incorporating MK was effective at delaying the age at failure. The best protection was offered at 15% MK; these specimens delayed cracking substantially when compared to the control specimen. For a chloride concentration of 3.03%, the control corrosion rate was calculated as 0.0058 mm/yr. The inclusion of MK slowed the corrosion rate as 0.0035 mm/yr and 0.0032 mm/yr for 5% MK and 15% MK, respectively. In general, the inclusion of MK reduced the corrosion rate by approximately 50%.

2.3.4.2 Alkali-Silica Reactivity

Ramlochan et al. observed that when MK was used, the expansion of the specimens decreased as the level of replacement increased [69]. In these studies, both the concrete prism and accelerated mortar bar tests were employed. The accelerated mortar bar method (ASTM C 1567) suggested a higher percentage of MK was needed to sufficiently mitigate ASR (around 15% MK), while concrete prism tests required only a 10% replacement by MK [70]. This is consistent with field studies that have reported a high rate of false positives while using the accelerated mortar bar method [71].

A substantial benefit from the use of pozzolans as a partial replacement for cement is their tendency to decrease the alkalinity of the pore solution and therefore increase the paste's ability to trap alkali ions which cause deleterious reactions. These reactions occur between reactive, siliceous aggregates and the alkali hydroxides that are present in cement. Ramlochan et al. performed an in-depth study on the ability of MK as a partial cement replacement to mitigate these effects through two separate reactive aggregates: a siliceous limestone and a greywacke-argillite gravel. In addition, paste mixtures were formed by mixing 10% and 20% MK with moderate and high-alkali cements. The MK that was studied was highly reactive ($SiO_2+Al_2O_3 = 97.35\%$), and the mixtures were held to a w/cm of 0.42–0.45 with no use of a HRWRA [69]. The concrete prism method that was used is similar to ASTM C1293, and the limit criteria was an expansion of less than or equal to 0.04%. The accelerated mortar bar method (ASTM C1260), modified for the addition of a pozzolan, was also conducted for concrete mixtures. For the paste mixtures, the pore solutions were expressed and analyzed over a two-year period to monitor various ion concentrations (OH-, Na+, and K+). The results showed that at seven days, all replacements displayed much lower pore solution alkalinity than the control pastes. Beyond seven days, the hydroxyl (OH⁻) ion concentration increased. The explanation is that at a 10% MK replacement, there is insufficient pozzolan to consume the calcium hydroxide produced during subsequent cement hydration.

A replacement of 20% MK does not show an increase in pore solution alkalinity. Furthermore, it is noted that the reduction in alkalinity by 10% MK is no more than would be observed from a 10% replacement by an inert material. However, the 20% MK replacement reduced the hydroxyl concentrations to less than 0.20–0.25 mol/l, which is

believed to be the threshold to maintain ASR [72]. The results of the concrete prism test indicated that the limestone aggregate at all replacement levels exhibited higher expansions than the greywacke-argillite gravel. At the age of two years, only the 20% MK replacement passed the limit criteria, while for the greywacke-argillite gravel, both 10% and 15% MK passed. According to the accelerated mortar bar method, only the 15% MK mixture passed the limit criteria of > 0.10% expansion at 14 days. This is inconsistent with the results from the prism method that indicated a 15% replacement as passing. The tendency of the mortar bar method to suggest that a higher level of replacement is needed has been documented in the literature [71].

Kostuch et al. was able to completely reduce expansion due to ASR by replacing 15% of OPC with MK. The expansive product was found to be a gel with high concentrations of Ca⁺ ions and was linked to the available CH/SiO₂ ratio. Thus, a primary mechanism by which ASR is mitigated by MK is the consumption of CH, which reduces the ability of expansive Ca⁺ gels to form.

Yazici et al. studied the effect of MK replacements for cement at 5%, 10%, 15%, and 20% abiding by the test methods as per ASTM C 1260 [55, 73]. As with their results for sulfate attack, the researchers found that the 5% MK mortars exhibited lower expansions than the control, but not as significantly as those containing 10%–20% MK [55]. Notably, the alkali present in MK cannot react with reactive silica and therefore does not contribute to the ASR acceleration. Furthermore, the CH being produced in cement hydration is quickly dissipated as it reacts with SiO₂ to form additional C-S-H gel, thereby reducing the available alkalis.

2.3.4.3 Sulfate Expansion

A similar study was conducted by Khatib and Wild on the influence of MK on the sulfate resistance of mortar bars. A replacement level of 15% MK was deemed necessary to provide good sulfate resistance.

Yazici et al. observed the effect of MK additions (5%, 10%, 15%, and 20%) on the sulfate resistance of mortars at a w/cm ratio of 0.50 and were performed as per ASTM C 1020 [34, 55]. According to ASTM C 1157, the six-month expansion limit is 0.1% of the original specimen length [74]. While all specimens fell below the limit at 180 days of curing, the mortars containing MK were significantly lower than the control mortar, with the 10% MK mortar being the optimum replacement level. These results were obtained using a sulfate concentration of 50 g/L Na₂SO₄. An experiment was also conducted at a sulfate concentration of 50 g/L Na₂SO₄, and, while the expansion values were higher than the previous test, even at high sulfate concentrations, mortars containing greater than 10% MK displayed expansions around half of the control mortar. The given explanations for the increased resistance toward sulfate attack are as follows: MK replacement of cement results in a decrease in C₃A, and the permeability decrease reduces ingress of sulfate ions into the pore solution.

2.3.4.4 Water Permeability

Barbhuiya et al. found that sorptivity decreased systematically with the addition of MK at a w/cm ratio of 0.50 but increased with successive MK replacements at a w/cm of 0.60 [54]. The authors attributes the decrease in sorptivity to three factors: the reduction in thickness of the ITZ due to CH consumption, the increase in number of discontinuous pores caused by the addition of MK, and the decreased porosity and finer pore structure that

results from the addition of MK. The authors speculated that the increase in sorptivity seen at a w/cm of 0.60 could be a result of the increased amount of free water in the mixture at the plastic state. This increase in water content may have provided for greater lubrication and hydration of cement particles, which would in-turn thicken the ITZ.

Yazici et al. performed water absorption tests on mortars of age 28-days for cement replacements by MK of 5%, 10%, 15%, and 20% at a w/cm ratio of 0.50 [55]. It was found that the mortars containing MK absorbed less water than the control mortar (7.8% of weight of specimen). Furthermore, as with compressive and flexural strengths, the optimum percentage was found to be 15% MK, with a low of 5.6% water absorption by weight of specimen.

Badogiannis et al. observed a decrease in sorptivity at all replacement levels. In addition, higher cement replacement levels (here 20%) demonstrated a substantial benefit, with the largest reduction at 20% MK (sorptivity 41.2% lower than the control). All mixtures had a w/cm ratio of 0.50 [57].

Guneyisi et al. found that at a w/cm ratio equal to 0.25, cement replacement of 15% by SF achieved the greatest decrease in sorptivity from the control [58]. However, at a w/cm ratio equal to 0.35, a 15% replacement of cement by MK was found to be optimal. The SF blended concretes displayed a much greater change in response to a changing w/cm ratio compared to gas permeability, while the MK blended concretes displayed consistency. At both w/cm ratios, the MK blended concretes reduced the sorptivity by 29%, while the SF blended concretes reduced the sorptivity by 20% and 30% at w/cm equal to 0.35 and 0.25, respectively.

Sorptivity is a desirable index for two reasons: 1) Its test methods closely resemble the manner in which concrete transports water (and therefore deleterious substances) in the field. 2) The test highlights the quality (or lack thereof) of the regions near the surface of the concrete, which determine the extent to which steel reinforcement is affected by the transport of various substances.

Ramezanianpour and Jovein studied the effects of varying replacement levels of cement by MK (control, 10%, 12.5%, and 15%). The replacement levels were also mixed for three separate w/cm ratios: 0.50, 0.40, and 0.35 [59]. The study found that the sorptivity coefficient was lowest at a 10% MK replacement at all ages up to 180 days. The general trends were that a decrease in w/cm resulted in a decreased sorptivity coefficient and that diminishing effects were observed as MK was added past 10%. In the case of the 0.40 w/cm mixture, the 15% MK replacement possessed sorptivity coefficients higher than the control at all ages. For the 0.35 w/cm mixture, the 12.5% and 15% MK replacements possessed sorptivity coefficients higher than the control at all ages.

2.3.4.5 Gas Permeability

Guneyisi et al. observed the effects on concrete by changing w/cm ratios and employing 5% and 15% replacements for cement by MK and SF [58]. The 0.25 w/cm ratio showed lower gas permeability of the two w/cm ratios. At a w/cm ratio equal to 0.25, the 15% MK blended concrete displayed the lowest gas permeability coefficient. However, at a w/cm ratio equal to 0.35, the 15% SF displayed the lowest gas permeability coefficient. The effectiveness of MK and SF at lowering the gas permeability varies at different w/cm ratios. The 15% MK reduced the gas permeability coefficient by 56% and 52% at w/cm ratios of 0.35 and 0.25, respectively. Meanwhile, the 15% SF reduced the gas permeability

coefficient by 61% and 50% for the same respective w/cm ratios. This indicates that MK and SF are similarly beneficial for reducing the gas permeability of concrete.

2.3.4.6 Carbonation

Carbonation is the dissolution of CO₂ into the pore solution of a concrete specimen which reacts with the CH to produce calcium carbonate (CaCO₃).

Barbhuiya et al. conducted carbonation indication tests by placing concrete specimens in a 5% CO₂ cabinet for a period of three weeks [54]. At the end of the three-week period, the specimens were split longitudinally, and the interior surface was sprayed with a phenolphthalein indicator solution. The metric used to detect the degree of carbonation was the depth of carbonation from the edge of the specimen. The research team found that at both w/cm ratios (0.50 and 0.60), the carbonation depth increased with higher replacements of MK with the exception of the 10% MK addition at a w/cm of 0.60. Thus the addition of MK affected carbonation depth of the 0.60 w/cm concrete more drastically, with very little effect by the MK addition up to 10% MK. This research indicated that the reduction in porosity may not have been able to counteract the detrimental loss of the CH in the pore solution.

2.3.5 Combination with Other SCMs

2.3.5.1 Metakaolin and Fly Ash

Saravanan studied concrete mixtures at a w/cm of 0.41 with a constant 10% fly ash (FA) and 5%–25% MK (in increments of 5%). Compressive cubes showed 10.82%, 29.75%, 55.16%, 72.14%, and 28.43% increases in compressive strength from a 5%, 10%, 15%, 20%, and 25% replacement by MK, respectively, while maintaining a 10% replacement by

FA. The highest strength was 58.66 N/mm² at a 20% replacement by MK [52]. The RCPT results after six hours of testing indicated that with increasing MK content, the charge passed decreased, especially after 10% MK. The control specimen passed 11,366 Coulombs, while the 15% MK 10% FA mixture passed 1,455 Coulombs. One-dimensional sorpitivity was also measured, which is the one-dimensional measure of capillary movement in a porous substance, and was found to systematically decrease as the percentage of MK increased.

Sabir et al. noted that in several studies where SCMs are known for low early strengths, the addition of MK was successful in providing similar or higher early strengths to that of the control mixture [30]. This is significant in that, while many SCMs are effective in improving durability and later high strengths, most SCMs also decrease early strengths. This indicates that, apart from FA, almost all SCMs could benefit from a further replacement by MK.

2.3.5.2 Metakaolin and Blast Furnace Slag

Khatib and Hibbert studied the combined effects of MK and ground granulated blast furnace slag (GGBS) at a w/cm of 0.50. The study showed that MK contributed to early strength up to a replacement level of 50% GGBS, but at higher replacements (70% GGBS), the rate of strength gain was similar to the control mixture [53]. This was true for both the 10% and 20% MK mixtures. It was also found that even at high replacements by GGBS, the addition of MK produced flexural strength comparable to the control. This is attributed to the denser and more efficient particle packing of the ITZ. Furthermore, the addition of MK produced compressive strengths higher than the control as early as one day of curing for up to 30% GGBS. Khatib and Hibbert noticed here that the MK replacement level

providing optimum compressive strength changed as the level of GGBS changed. With no MK, the optimum replacement by GGBS was 50% [53]. Similarly, for the 10% and 20% MK concretes, the optimum replacements by GGBS were found to be 30% and 20%, respectively. The explanation for this is the tendency of both MK and GGBS to reduce both the Ca/Si ratio and pH of the pore solution. Because the MK reacts much earlier than the GGBS, with high MK contents, some compounds in the GGBS may not react and will therefore display a reduction in strength.

Asbridge et al. examined concretes containing both MK and GGBS and found that at each GGBS replacement level, MK reduced the frequency of large pores. In addition, large increases in compressive strength were seen at 96 days when compared to the control. The authors therefore concluded that the improved pore properties, the removal of excess CH, and the reduction in diffusion over primary GGBS concrete imply that this ternary mixture produces more durable concretes.

Li and Ding noticed that, although the addition of GGBS tends to increase the workability of a concrete mixture, ternary blends with MK and GGBS are less fluid than control mixtures [46]. The GGBS used in this study was an "ultra-fine" slag with a Blaine specific surface area of 630 m²/kg. As a comparison, the MK used in this study had a Blaine specific surface area of 310 m²/kg. The binary MK mixture was found to decrease both initial and final setting times, while all ternary mixtures of MK and GGBS saw an increase in setting times compared to the control. The compressive strengths of specimens were also taken at 3, 7, and 28 days of curing. While the binary MK and OPC mixtures' strengths were higher at 3 days, by 7 days the MK and GGBS mixtures surpassed them. By 28 days of curing, the MK and GGBS mixtures' compressive strengths far exceeded the binary MK

and OPC mixtures. X-ray diffraction (XRD) indicated that the binary MK [46] and 10% MK with 30% GGBS mixtures contained a higher concentration of AFt phases at 28 days of curing. XRD results also showed that the 10% MK with 30% GGBS mixture displayed the lowest CH content. This is because both MK and GGBS take part in the pozzolanic reaction that consumes CH.

Nasir et al. observed that ternary blends of MK and GGBS produced a heat of hydration less than OPC mixtures [75].

Justice and Kurtis utilized calorimetry to observe the effect of MK on heat evolution and cumulative evolved heat. The first hydration peak of the heat evolution (J/g, typically corresponding to C₃S hydration) was lower than the control, while the second hydration peak (typically corresponding to the C₃A hydration) showed a marked increase over the control [51]. The authors believed that this increase is indicative of an acceleration of the C₃A hydration, pozzolanic exothermic reactions, or delayed solution of the MK. A maximum in both heat evolution and cumulative heat evolved was observed with the finer MK, indicating that MK material fineness influences the rate of reaction and that the reactions resulting from the inclusion at MK are exothermic in nature.

2.3.6 Additional Information

2.3.6.1 Heat of Hydration

Snelson et al. found that the rate of heat evolution (J/gh) occurring within the first hour of hydration (pre-induction period of hydration) was decreased with the addition of MK in cement paste [76]. This decrease was especially prominent in the 10% and 15% replacements and can be attributed to the reduction in water by the MK. MK's high specific surface area promotes mass absorption of the water, which delays hydration of the cement.

Similar trends can be seen at one–eight hours of hydration, where the cumulative heat of hydration (J/g) for all MK replacement levels is lower than that of the control. At 120 hours, however, the cumulative heat of hydration of the 15% MK system had surpassed the control system, with the other replacement levels still increasing as well with respect to the control. Interestingly, this 15% replacement had a higher cumulative heat of hydration that the 20% MK, marking a non-systematic increase of liberated heat with respect to replacement level. The explanation for this can be found when attention is paid to the amount of available Ca²⁺ ions. The reduction in cement results in the reduction of produced CH, which in turn limits the pozzolanic reaction of the MK while also replacing greater amounts of cement. This supports the idea that the amount of MK needed to completely consume the available CH is 15%–20%.

Jiang et al. utilized isothermal calorimetry to quantify the liberated heat of mortars incorporating MK at a w/cm ratio of 0.17 [13]. Measurements were taken up to 100 hours, where 6% MK corresponded to the highest cumulative heat of hydration at 103.32 Joules, and 14% MK corresponded to the lowest at 91.58 Joules. These results seem to support the explanation that up to a point, the combined effects of the acceleration of cement hydration by the MK and the pozzolanic reaction of the MK result in a greater liberation of heat. After this point, the dilution effect results in a net reduction in the heat of hydration.

2.3.6.2 CH Consumption, Pozzolanic Activity, and Metakaolin Chemistry

Paiva et al. studied the consumption of the calcium hydroxide (CH or Ca(OH)₂) produced during cement hydration by the MK and found that with increasing MK, the free CH was consumed. The control at a w/cm of 0.60 contained 11.9% CH by mass of cement, while the 30% MK concrete contained 1.6% [44].

The reactivity of thermally treated and mechanically treated kaolins was studied by Fitos et al. using the Chapelle test. This index represents the amount of CH consumed in grams per gram of MK. The study indicated that mechanical activation of kaolin is competitive with respect to reactivity to that of thermal activation [26]. Furthermore, the study found that the percentage of kaolinite guides the level of reactivity between different kaolins.

Subasi and Emiroglu performed pozzolanic reactivity tests on a low-reactivity MK according to ASTM C311 [31, 49]. The results indicated that the pozzolanic activity of mortars at a 20% MK replacement changes over time, with the pozzolanic activity of 77% at 7 days of curing and 82% at 28 days.

Subasi and Emiroglu performed XRD on pastes with 0%–30% MK and found a decrease in CH in all pastes containing MK. The reduction was minimal at 5% and more significant at all other replacement levels. In addition, 10%–30% replacements seemed to have comparable CH peaks, indicating that low-pozzolanic activity corresponds to a lack of ability to consume additional CH past a 10% MK addition [49]. It is also worth noting that the C-S-H content decreased initially at a 5% MK replacement and increased from there up to 30% MK. The amount of C-S-H was ultimately lower than the control mixture.

In a review, Sabir et al. stated that fully-hydrated OPC produced CH up to 20% of its own weight in practice. When in the presence of CH, pozzolanic materials (including MK) form hydration products in addition to the C-S-H formed during cement hydration [30]. Some of these products are additional C-S-H gel, calcium aluminate hydrates, and alumino-silicate hydrates (e.g., C₂ASH₈, C₄AH₁₃, and C₃AH₆). According to Sabir, the formation of crystalline products primarily depends on the Al₂O₃·2SO₂ / Ca(OH)₂ (AS₂/CH)

contents [30]. Furthermore, the types and amounts of hydration products depend heavily on OPC composition, MK purity, and w/cm ratio. This review further reported that an MK replacement level "considerably in excess of 15%" is required to fully consume the CH produced during cement hydration. A notable minimum in CH content was observed by Wild and Khatib at 14 days of curing, indicating that at this age the rate of CH consumption by MK is much greater than the rate of CH production by the OPC.

Coleman and Page showed that up to a replacement level of 20% MK, the Cl⁻ to (OH)⁻ ratio in the pore solution was comparable to that of OPC mixtures. Thus although a decrease in pore solution pH was observed, a replacement level up to 20% may not be significant in reducing the risk of chloride induced corrosion of reinforcing steel.

The primary cementitious reaction observed within MK concretes is the formation of C-S-H gel, which is the byproduct of the amorphous or glassy silica reacting with the CH produced in cement hydration [30]. MK, which also contains a high percentage of Al₂O₃, also forms hydration products such as CAH and CASH which are believed to assist in the cementitious process and contribute to strength.

Barbhuiya et al. noted that the reduction in ettringite XRD peaks at 28 days of curing is likely the result of calcium sulphoaluminate transforming into a more stable calcium aluminate hydrate, which takes the form of cubic crystals in the hydrated paste [54]. This study also indicated that the relative proportions of C-S-H gel are affected by the inclusion of MK [54]. According to nanoindentation results, the addition of MK promoted the formation of low-density and high-density C-S-H gel over the loosely-packed C-S-H gel.

Justice and Kurtis utilized DTA and thermogravimetric analysis (TGA) along with MKs of different fineness to analyze the consumption of CH inside paste specimens. An increased amount of CH relative to the control at early ages of hydration (~8 hours) indicated that cement hydration is accelerated by including MK [51]. A decrease in CH content from 7 to 28 days of hydration also indicated that the pozzolanic reaction continues to consume more CH than is produced after 7 days. Interestingly, the material fineness affected the consumption rate of CH. Finer MK consumed CH at faster rates at early ages, but coarser MK consumed more CH by the 28-day mark. Generally, a reduction in CH is accompanied by higher strengths, as the CH is not a significant contributor to concrete strength. Similarly, a decrease in CH content provides less of a likelihood that the CH will later participate in leeching or deleterious reactions.

Scanning electron microscope (SEM) photographs illustrated that the inclusion of SCMs increased the uniformity of the paste surrounding the aggregates and decreased the size and frequency of microcracks. In addition, the SEM micrographs showed that the addition of SCMs resulted in a reduction of ettringite crystals and an increase in C-S-H and C-A-S-H gels.

Duan et al. numerically modeled the OPC hydration (silica-free system) and the hydration reaction of cement and SCM combinations. The researchers found that in the OPC system, monosulfoaluminate was more stable than the phase assemblage of ettringite and C_3AH_6 at temperatures > 5°C [60]. However, when silica was introduced via an SCM, the phase assemblage of ettringite and $C_3AS_{0.8}H_{4.4}$, which is a member of the solid solution C_{3A}

assemblages were more thermodynamically stable when SCMs were used in concrete mixtures.

2.3.6.3 Pore Properties of Metakaolin Concrete

Poon et al. utilized Mercury Intrusion Porosimetry (MIP) in the attempt to correlate increases in mechanical strength and durability to the pore density of MK concretes. They found that at a w/cm of 0.30, the MK reduced the average pore diameter and the MIP porosity [29]. These changes correlated with increases in compressive strength, especially at early ages, as well as with the reduction in the chloride ion transport at all ages.

Jiang et al. also measured pore size distribution using MIP and found that all MK replacement levels resulted in a porosity of less than 15% at a w/cm ratio of 0.17 [13]. As compared to FA and SF, MK has a course and irregular particle surface which has a higher yield stress and viscosity and therefore entrains more air. Accordingly, these rheological parameters should increase with a decrease in workability, and this relationship is consistent with the findings of Paiva et al. [44].

A literature review by Sabir et al. indicated that average pore size decreased with the addition of MK [30]. Specifically, a study conducted by Bredy et al. demonstrated that at a replacement level of 30%, the pores were typically narrow-necked pores with a diameter of less than 0.03 µm [77]. Barbhuiya et al. found a reduction in porosity resulted from a 10% MK specimen, at a w/cm of 0.40, over the control [54].

Badogiannis et al. measured the porosity and mean pore size in concretes containing 10% and 20% MK replacement levels. The mean pore size was reduced for all replacement levels of MK, and the porosity was lower, as well [57]. A maximum reduction in average pore size was observed when using a 20% replacement of cement by commercial-grade

MK. This mixture, however, did not correspond to the largest reduction in porosity, which was found in the mixture with a 10% replacement of cement by a poor Greek kaolin.

SEM images taken by Ramezanianpour and Jovein indicated that by 28 days of curing, pastes containing MK were more compact and uniform. These characteristics were not as evident at seven days of curing. A reduction in the frequency of ettringite crystals was also observed, replaced by additional calcium silicate hydrates and calcium aluminosilicate hydrates [59]. Further, XRD was performed on paste samples, and its findings supported the reduction in CH and the increase in quartz.

Justice and Kurtis investigated the pore properties of pastes containing MK using nitrogen adsorption tests. The percentage of fine pores (<10 nm) increased with the addition [51]. Furthermore, a finer pore structure was observed with the finer MK than the coarser MK—63%, 57%, and 43% for the finer MK, coarser MK, and the control, respectively.

Duan et al. performed MIP, microhardness tests, and SEM on the ITZ of concrete specimens containing GGBS, SF, and MK. In addition, thermodynamic modeling was performed to gain insights into the change in prevalence of hydration products when using the aforementioned SCMs. MIP results indicated that the overall porosity decreased with the addition of all SCMs while the average pore diameter decreased with respect to the control. In decreasing order of effectiveness of the SCMs were MK, SF, and GGBS [60]. Fine SCM particles can be seen to fill gaps between cement particles, densifying the paste matrix. Additional C-S-H gels form due to pozzolanic reactions and optimize the microstructure of the concrete. Microhardness tests were performed on the ITZ of concrete specimens containing SCMs. As the aggregate interface is approached in OPC concretes,

the porosity increases and the prevalence of CH here decreases strength. The results of the microhardness tests showed that the inclusion of SCMs increased the strength of this region. Microhardness can also be seen to increase with curing time, as is expected with OPC concretes.

2.4 Summary of Findings Relevant to This Study

Table 5 summarizes the findings from the literature review, which are directly relevant to the research study.

Table 5 – Summary of literature review.

Property	Relative to Control	Sources
Workability	Decrease	Paiva et al. (2012)
		Caldarone et al. (1994)
Setting Time	Increase	Brooks et al. (2001)
		Subasi & Emiroglu (2015)
Compressive Strength	Increase	Khatib & Hibbert (2005)
		Sabir et al. (2001)
		Barbhuiya et al. (2015)
		Yazici et al. (2014)
Tensile Strength	Increase	Jiang et al. (2015)
		Yazici et al. (2014)
		Subasi & Emiroglu (2015)
Modulus of Elasticity (MOE)	Increase	Dinakar et al. (2012)
Alkali Silica Reactivity	Decrease	Ramlochan et al. (2000)
		Kostuch et al. (1993)
Permeability (Cl ⁻ , water, gas, etc.)	Decrease	Poon et al. (2005)
		Tafraoui et al. (2016)
Shrinkage & Creep	Decrease	Brooks et al. (2001)
		Wild et al. (1998)
Sulfate Resistance	Increase	Yazici et al. (2014)
Heat of Hydration	Decrease/	Meland et al. (1983);
	Increase	Alshamsi (1997); Bentur and
		Goldman (1988)

3. TEST PROCEDURES

3.1 Design of Experiment

Fly ash is a versatile SCM in that it can improve the fresh properties of concrete, boost mechanical strength, increase durability, and reduce liberated heat in mass concreting [5]. Because of its versatility, fly ash is widely used. The test regime should therefore explore the wide range of cement replacements typical of fly ash. Binary and ternary SCM combinations will be evaluated for this purpose.

In this study, the following concrete mixtures—including binary and ternary cement replacements with MK—are considered: product No. 1 (MetaMax), product No. 2 (PowerPozz), product No. 3 (Kaorock), and slag product 'a' (Agros' Grade 120) and product 'b' (Lehigh Hanson's Cape Slag).

3.1.1 Design of Mixtures

Nineteen unique combinations of SCMs were evaluated, including an OPC control mixture. Three commercial MK products were evaluated as binary replacements of cement. Each product replaced cement by 10%, 15%, and 20% by weight. In addition, three ternary mixtures including MK and slag were studied. This replacement of cement amounted to 15% by each MK and 30% by a slag. The slag product was the same for these three mixtures so that the behavior of each MK with slag could be compared. One MK product was also part of a ternary mixture with another commercially available slag in order to observe behavior differences of an MK with different slags. Finally, three binary mixtures were performed, including the two aforementioned slags, as well as a high-volume fly ash

mixture. These served as additional benchmarks to evaluate the performance of the MK mixtures.

3.1.2 Design of Tests for Mechanical and Durability Evaluation

Each of the 19 SCM combinations were tested for fresh and hardened concrete properties. Temperature, slump, unit weight, and air content were measured at the time of batching. Tests of mechanical strength included compression, split-tension, and MOR. The static MOE via compression, as well as the dynamic MOE via sonic resonance were measured. Indirect tests of durability and resistance to chemical attack were conducted, as well. These tests included drying shrinkage, chloride-ion permeability, resistance to sulfate attack, and resistance to alkali-silica reactions. Shrinkage induced cracks can compromise the structural integrity and durability of concrete structures by providing easy access channels for water to carry chloride ions to the steel reinforcement and cause corrosion. Therefore, a dry shrinkage test was presented as part of the durability evaluation. Tests will be covered in greater detail in Section 3.3, and a summary of all testing methods used can be found in Table 6.

Table 6 – Summary of SCM combinations investigated.

Name	Fresh/Hardened	Mechanical/ Durability	Concrete/ Mortar	Testing Standard Used	
Temperature	Fresh	-	Concrete	ASTM C1064	AASHTO T 309
Slump	Fresh	-	Concrete	ASTM C143	AASHTO T 119
Air Content	Fresh	-	Concrete	ASTM C231	AASHTO T152
Unit Weight	Fresh	-	Concrete	ASTM C138	AASHTO T 121
Compression	Hardened	Mechanical	Concrete	ASTM C39	AASHTO T 22
Split-Tension	Hardened	Mechanical	Concrete	ASTM C496	AASHTO T 198
MOR	Hardened	Mechanical	Concrete	ASTM C78	AASHTO T 97
Static MOE	Hardened	Mechanical	Concrete	-	-
Dynamic MOE	Hardened	Mechanical	Concrete	-	-
CTE	Hardened	Mechanical	Concrete	-	AASHTO TP 60
Drying Shrinkage	Hardened	Mechanical	Concrete	ASTM C156	AASHTO T 160
RCPT	Hardened	Durability	Concrete	ASTM C1202	AASHTO T 277
Sulfate Expansion	Hardened	Durability	Mortar	ASTM C1012	
ASR Expansion	Hardened	Durability	Mortar	ASTM C 1567	AASHTO T 303

3.2 Materials

Three MK products were evaluated: MetaMax by BASF, sourced from Sandersville, Georgia; PowerPozz by Advanced Cement Technologies (ACT) sourced from Aiken, South Carolina; and KAOROCK by Thiele Kaolin Company sourced from Sandersville, Georgia. All MK products used in this study are high reactivity metakaolins (HRMs) that conform to ASTM C 618 [22]. The consensus within the literature is that a HRM is any MK that contains $SiO_2 + Al_2O_3 + FeO_2 \ge 90\%$ by weight. As all MK evaluated in this study are HRMs, they are simply referred to as MKs. Although the reactivity of any MK is primarily dependent on the percentage of kaolin that is dehydroxylated during calcination, this information is not typically available on technical data sheets provided by commercial MK companies. However, technical data sheets typically contain a breakdown of oxides by weight and material fineness. Together, these two parameters are good predictors of

quality. A combination of physical and chemical characteristics of the MK used in this study are found in Table 7. Pictures of each product are shown in Figure 7.

Table 7 – Chemical & physical properties of MK products.

	Description	Product No. 1	Product No. 2	Product No. 3	
	SiO ₂	50.75%	54%-56%	51.66%	
S	Al ₂ O ₃	45.91%	40%-42%	43.99%	
Chemical Properties	Fe₂O₃	0.45%	< 1.4%	0.47%	
obe	Cao	0.06%	< 0.1%	0.01%	
l Pr	MgO	0.00%	< 0.1%	0.03%	
)ica	Na₂O	0.23%	< 0.05%	1.89%	
hen	TiO₂	1.87%	< 3%	1.89%	
ט	SO₃	0.08%	< 0.05%	-	
	LOI	0.42%	< 1.0%	0.50%	
	Specific Gravity	2.6	2.6	2.5	
erties	Specific Surface (Blaine)*	Not specified	26000 cm2/g	Not specified	
Physical Properties	Specific Surface (BET)*	Not specified	20 m2/g	11 m2/g	
Physic	Fineness (Retained on #325 Sieve)	0.00%	Not specified	0.10%	

^{*} Note: All 3 products contain $SiO_2 + Al_2O_3 + FeO_2 \ge 95\%$ by weight.



MK product No. 1: MetaMax (by BASF)



(b) MK product No. 2: PowerPozz (by ACT)



(c) MK product No. 3: PowerPozz (by Thiele)

Figure 7 - MK products No. 1, 2, and 3 from left to right.

Table 8 – Chemical and physical properties of Portland cement for all mixtures.

	Descr	ription	Type I/II
		SiO ₂	19.70%
	10	Al ₂ O ₃	4.70%
	des	Fe ₂ O ₃	3.00%
	Properties Weight by Oxides	Cao	63.30%
ies	, by	MgO	3.10%
perl	sert Bht	Na₂O	-
Chemical Properties I Weight by	TiO ₂	-	
		SO₃	3.20%
mi		LOI	2.70%
Che	se Sn	C₃S	54.00%
	lcate Pha ositic	C ₂ S	15.00%
	Calculcated Bogue Phase Composition	C₃A	7.00%
	ນ ອີ	C ₄ AF	9.00%
	Physical Properties	Specific Gravity	3.16
	ορ	Specific	387 m ² /kg
	<u>P</u>	Surface Area	307 III / Kg
sica		Fineness	
	λγ	(Retained on	-
	<u> </u>	#325 Sieve)	

A Type I/II Portland cement conforming to ASTM C150 was used for all concrete and mortar mixtures. The cement was provided by Argos and is local to Atlanta, Georgia. Table 8 lists its physical and chemical characteristics, and the Bogue-calculated phase composition is provided in Table 8.

Two Grade 120 commercially available slags were donated to the study. The first was provided by Argos and the second by Lehigh Hanson. In this report, the products are referred to as product 'a' and product 'b,' respectively. As with MK, oxide composition and physical characteristics are important in understanding the behavior of these products once inside the concrete. These can be found in Table 7. The fly ash was donated by Boral

USA and is an ASTM C618 Class F fly ash. Pertinent physical and chemical properties for the fly ash and slag products are also included in Table 9.

Table 9 – Chemical and physical properties of other SCMs used in study.

	Description	Slag product 'a'	Slag product 'b'	Fly Ash	
	SiO₂	33.33%	34.07%	50.77%	
S	Al ₂ O ₃	13.50%	12.73%	26.65%	
rtie	Fe₂O₃	0.68%	0.47%	3.76%	
Chemical Properties	Cao	41.28%	40.41%	11.30%	
P P	MgO	5.53%	6.56%	2.15%	
ica	Na₂O	0.21%	0.17%	1.17%	
hen	TiO₂	1.89%	0.52%	-	
ᄓ	SO₃	2.30%		1.20%	
	LOI	Not specified	1.05%	-	
	Specific Gravity	2.80	2.87	2.53	
erties	Specific Surface (Blaine)*	472 m2/g	531 m2/g	Not specified	
Physical Properties	Specific Surface (BET)*	Not specified	Not specified	Not specified	
Physic	Fineness (Retained on #325 Sieve)	3.00%	Not specified	Not specified	

Aggregates conforming to both ASTM C33 and GDOT requirements were used in all concrete and mortar mixtures. The coarse aggregate is a locally sourced from Hanson Aggregates East in Athens, Georgia, and the fine aggregate is sourced from Redland Sand in Watkinsville, Georgia. The course aggregate is a standard size #57 (NMAS 1") graded Granite Gneiss/Amphibolite stone. The fine aggregate is an alluvial river sand. Gradations performed on both can be found in Figures 8–12. Water used for mixing was tap water. Finally, a PCE-based (polycaboxylate ether - BASF's MasterGlenium 7920) superplasticizer was used for all mixtures.

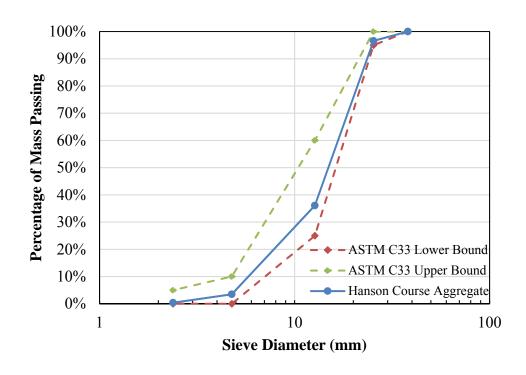


Figure 8 – Comparative sieve analysis of coarse aggregate to ASTM C33 specifications.

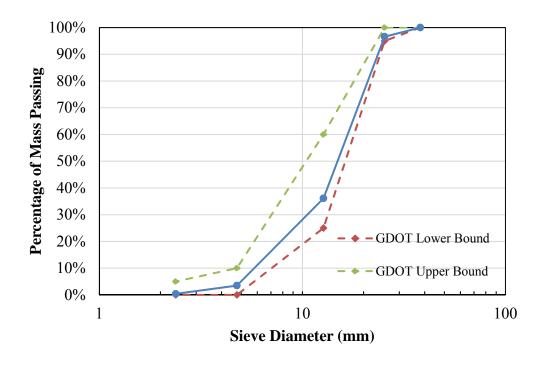


Figure 9 – Comparative sieve analysis of coarse aggregate to GDOT specifications.

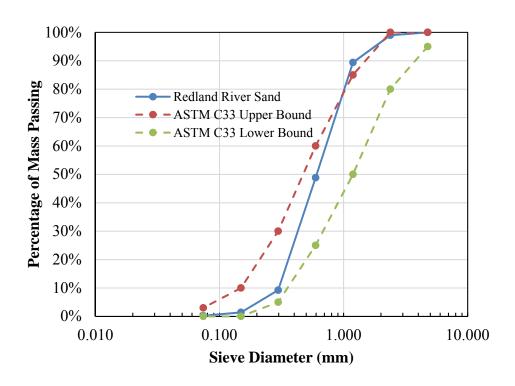


Figure 10 – Comparative sieve analysis of fine aggregate to ASTM C33 specifications.

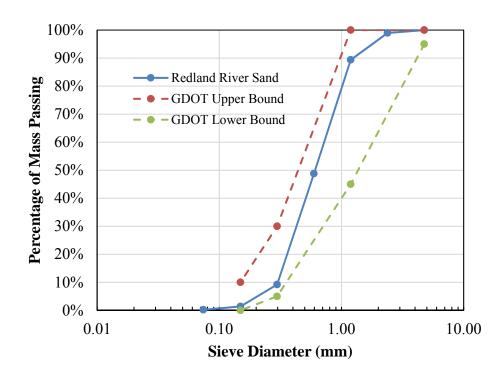


Figure 11 – Comparative sieve analysis of fine aggregate to GDOT specifications.

3.3 Testing Methods and Procedures

3.3.1 Mixture Design

3.3.1.1 Mixture Proportions

Concrete mixture proportions are based on a GDOT drilled shaft design that incorporated a high volume of fly ash to reduce heat of hydration and cost. The mixture design can be found in Table 10. The total cementitious materials for each mixture is 711 pcy. The water-to-cementitious materials ratio (w/cm) is 0.43, and the course aggregate fraction is 1,660 pcy. All concrete mixtures incorporate air content equal to 4%. SCMs replace a percentage of cement by weight. As for the weight of sand, mixtures were proportioned according to the absolute volume method as in ACI 211. Saturated surface-dry (SSD) mixture proportions are found in Table 11.

The dosage of superplasticizer (MasterGlenium 7920 by BASF) varies by mixture, as each mixture has different water requirements and consistent workability is desired. Dosages were altered to attain a target slump of 2"-6" and an air content of 3%-6%. These target ranges correspond to upper and lower limits for structural concrete as outlined in Section 500 of GDOT Standard Specifications.

Table 10 - Reference mixture - GDOT drilled shaft mix.

Drilled Shafts Mix - GDOT						
f'c ~ 3500 psi	Proposed	Mix (Per CY)				
Material	Weight Volume					
Cement	391 lb.	1.99 cf				
Fly Ash (Class F)	320 lb.	2.23 cf				
Course Aggregate	1660 lb.	7.37 cf				
Fine Aggregate	1210 lb.	10.08 cf				
Water	306 lb.	5.06 cf				
Entrapped Air	-	1.00%				
BASF Poly 997	10 oz./cwt					
BASF Poly Z 60	6 oz./cwt					
BASF Delvo	12 oz./cwt	•				

Table 11 – SSD mixture proportions for concrete mixtures.

r	Mixture Code	Cement (pcy)	Metakaolin (pcy)	Slag (pcy)	Fly Ash (pcy)	Course Aggregate (pcy)	Fine Aggregate (pcy)	Water (pcy)	Air (%)	Superplasticizer (oz. / 100 lb cm)
M1	CON	711	0	0	0	1660	1218	306	4.00%	3.3
M2	MK1-10	640	71	0	0	1660	1205	306	4.00%	6.8
М3	MK1-15	604	107	0	0	1660	1199	306	4.00%	6.7
M4	MK1-20	569	142	0	0	1660	1193	306	4.00%	7.6
M5	MK2-10	640	71	0	0	1660	1205	306	4.00%	6.5
М6	MK2-15	604	107	0	0	1660	1199	306	4.00%	7.1
M7	MK2-20	569	142	0	0	1660	1193	306	4.00%	7.9
M8	MK3-10	640	71	0	0	1660	1205	306	4.00%	6.4
М9	MK3-15	604	107	0	0	1660	1199	306	4.00%	7.5
M10	MK3-15	569	142	0	0	1660	1193	306	4.00%	8.2
M11	MK1-15_SLa-30	391	107	213	0	1660	1183	306	4.00%	7.3
M12	MK1-15_SLa-30	391	107	213	0	1660	1183	306	4.00%	7.0
M13	MK1-15_SLa-30	391	107	213	0	1660	1183	306	4.00%	7.0
M14	MK1-15_SLb-30	391	107	213	0	1660	1183	306	4.00%	7.3
M15	MK2-15_SLb-30	391	107	213	0	1660	1183	306	4.00%	7.3
M16	MK3-15_SLb-30	391	107	213	0	1660	1183	306	4.00%	7.0
M17	SLa-30	498	0	213	0	1660	1202	306	4.00%	3.4
M18	SLb-30	498	0	213	0	1660	1202	306	4.00%	4.1
M19	FA-45	391	0	0	320	1660	1118	306	4.00%	0.8

Mortar mixtures were produced for the ASR and sulfate tests. These tests require specific mixture proportions. In addition, a superplasticizer was used to overcome the increased water demand from fine SCMs. Specifically, the dosages found in Table 11 for concrete mixtures were used for mortar mixtures, as well. This addition of a

superplasticizer is a deviation from the accepted standard for the sulfate tests (ASTM C1012), in which an alteration of the w/cm ratio is specified. The choice to deviate from the standard was made because increasing the w/cm ratio has shown to diminish the benefits of MK. The SSD mixture proportions are mixed per the following criteria:

Sulfate

- o 1 part Portland cement to 2.75 parts sand by mass
- o w/cm = 0.485
- o replace percentage of Portland cement by SCM by weight
- → Ensure enough mortar for 6, 1"×1"×11.25" (25mm×25mm ×286mm), bars per mixture

ASR

- o 990g sand
- o 440g cementitious material
- o w/cm = 0.47
- → Make enough mortar for 3, 1"×1"×11.25" (25mm×25mm ×286mm), bars per mixture

3.3.1.2 Batching

Concretes were machine mixed using a Workman II Multimixer portable drum mixer (Figure 12) with a 12.5 cf capacity, in accordance with ASTM C192. SSD mixture proportions were altered to accommodate the current moisture conditions of the aggregates and then weighed using a scale with a 300 lb. capacity and 0.1 lb. accuracy. The coarse and fine aggregates, along with the cement, were added to the rotating mixer first and allowed to mix for two–three minutes. Once the mixture looked fairly homogenous, the SCMs were

added while the mixer continued to rotate. All dry materials were then mixed for approximately four—five minutes. The superplasticizer was added to the mixing water and thoroughly agitated before the water was added to the mixer. After all materials had been added, the mixer was allowed to rotate for another three minutes, followed by a two-minute rest period, and then followed by a final two-minute mixing period. The contents of the mixer were then discharged into a wheelbarrow so that fresh concrete tests could be performed and molds could be filled. Procedures for measuring fresh concrete properties are discussed in Section 3.3.2, and procedures for making specimens for various hardened concrete tests are discussed in Section 3.3.



Figure 12 – Portable drum mixer used to batch concrete mixtures.

Mortar mixtures used a KitchenAid mixer (Figure 13) to attain a uniform plastic consistency. As with the concrete mixtures, mixture proportions were altered to accommodate deviations from SSD aggregate conditions. Batching of all mortar followed the procedure outlined in ASTM C305. A mixture of Portland cement and SCMs was added to the bowl and allowed to mix until homogenous. During this process, a superplasticizer dosage (same as corresponding concrete mixture) was added to the mixing water and agitated. The mix water was then added to the bowl while the paddle continued to rotate, and the paste was allowed to mix for 30 seconds. The sand was then added slowly over a 30-second period, while the mixer speed was increased. While stopping the mixer for 90 seconds, the sides of the bowl were scraped down to allow any clumped material to mix again for a subsequent 60 seconds. The fresh properties of the mortar were not measured; however, mortar bar molds were filled for both ASR and sulfate tests.



Figure 13 – KitchenAid mixer used in batching mortar.

3.3.1.3 Fresh Properties

Concrete temperature, unit weight, air content, and slump were measured directly after batching. A thermometer accurate to 1 °F was used to record the temperature per ASTM C1064. Unit weight and air content were measured as outlined in ASTM C138 and C231, respectively. Slump was measured in accordance with ASTM C143.

3.3.2 Mechanical Properties

3.3.2.1 Compressive Strength

Nine 4"×8" compression cylinders were made upon each batching; three for each 1-day, 7-day, and 28-day strengths. They were cured in a lime saturated bath (see Figure 14) until the day of testing per ASTM C511. At the age of 1, 7, and 28 days, 3 cylinders were tested in a Forney universal testing machine with a capacity of 800,000 lbs. Cylinders were loaded at a rate of 35 psi/s (440 lb/s) until fracture. The average of three specimens was recorded for each of the three days. An image of a cylinder being tested can be seen in Figure 15.



Figure 14 – Lime saturated water in curing tanks for concrete specimens (maintained at 70° F).



Figure 15 – Compression cylinder being tested in Forney universal testing machine.

3.3.2.2 Tensile Strength

Two tests of tension were performed. The first was split-cylinder, which was tested after 28 days of curing and using cylinders of the same dimension as in the compression test per ASTM C496. The loading rate was 2.5 psi/s. The average results of three specimens was taken as the splitting-tensile strength. Before testing, cylinders were cured in a lime saturated bath per ASTM C511. The second test was the MOR test, which is a test of flexural strength. Three prisms (6"×6"×22") were cast at batching and prepared in accordance with ASTM C192. They cured in a lime saturated bath until the age of 29 days when they were removed and tested in a Forney universal testing machine. The average of three breaks was taken as the MOR. Figure 16 shows the setup.



Figure 16 – Setup for MOR tests.

3.3.2.3 Modulus of Elasticity

The MOE was measured per ASTM C469/469M.

3.3.2.4 Coefficient of Thermal Expansion

The coefficient of thermal expansion was measured for three 4"×7" cylinders after curing for 28 days. The cylinders were cast and cured just as the ones for compression and splittension. The cylinders were cut to a height of 7" from 8" by the use of a CC800M CoreCut diamond-tipped saw at an age of 27 days and returned to the curing tank for 1 additional day before testing. Cylinders were tested two at a time in a Pine Instruments CTE testing

machine (Figure 17) for a duration of 18 hours per AASHTO T336. The CTE was taken as the average CTE of three cylinders.



Figure 17 – Pine Instruments CTE testing machine.

3.3.3 Durability

3.3.3.1 Drying Shrinkage

Drying shrinkage was performed in accordance with ASTM C157. Three 4"×4"×11.25" rectangular prisms were cast at the time of batching and cured in a lime saturated bath after being released from the molds at 24 hours of age. While curing, relative length measurements were made at ages of 1, 3, 7, 14, and 28 days. At an age of 28 days, the prisms were removed from the bath and allowed to air dry on a shelf while being supported at either end by wooden blocks (Figure 18). Drying shrinkage measurements were taken at concrete ages of 32, 35, 42, 56, 84, 140, and 252 days using a length comparator (Figure

19). Length change as a percentage of the nominal gauge length (10") were calculated and reported as the average percent change of the three prisms.



Figure 18 – Drying shrinkage specimens supported at either end by wooden blocks.



Figure 19 – Length comparator used in drying shrinkage, ASR, and sulfate tests.

3.3.3.2 Rapid Chloride-Ion Permeability

Permeability was tested indirectly per ASTM C1202. Two cylinders with the same dimensions as the compression and split-tension cylinders were cast at batching and allowed to cure for 27 days. They were then pulled out of a lime saturated bath, and the topmost 2" were cut off using a diamond-tipped saw. They were returned to the bath and allowed to cure for an additional 24 hours. The specimens were then prepped by being subjected to vacuum pressure for one hour. At the end of the hour, boiled water was allowed to flood the vacuum chamber. The specimens lay immersed and under the remaining vacuum pressure for three hours. The chamber was then left undisturbed for 22 hours. RCPT was then performed for a duration of six hours per ASTM C1202. Aqueous solutions of NaOH and NaCl were made with concentrations of 12 g/L of solution and 30 g/L of solution, respectively. De-ionized water was used for the solutions. Figure 20 shows the Germann instruments testing equipment used to measure the total charge passed during the test.

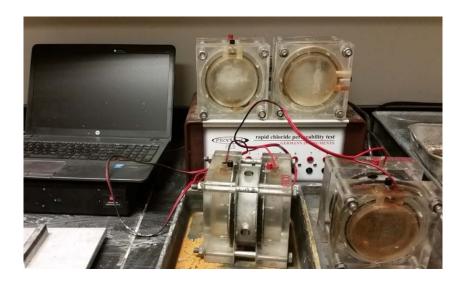


Figure 20 – RCPT testing equipment by Germann instruments Inc.

3.3.3.3 Resistance to Sulfate Attack

Resistance to sulfate attack was measured as specified by ASTM C1012. Six mortar prisms (1"×1"×11.25") and six mortar cubes were batched and stored at 95 °F for 24 hours. The specimens were then released, their lengths measured, and immersed in a lime saturated bath. The cubes were periodically tested per ASTM C109 until two cubes averaged above 2,850 psi. Once the cubes tested above the required strength, they were immersed in plastic containers with 0.75 L of aqueous NaSO4 solution per mortar bar. The concentration of NaSO4 was 40 g/L of solution. Measurements were taken at standardized ages of 1, 2, 3, 4, 8, 13, and 15 weeks after initially immersed in solution. At each of the standard intervals, the solution was replaced. Expansion was measured as percentage of length change. Figure 21 displays bars in the aqueous solution.



Figure 21 – Sulfate mortar bars in solution.

3.3.3.4 Resistance to Alkali-Silica Reaction

ASR was tested per ASTM C1567. Three mortar bars per mixture were batched in order to measure expansion by a caustic aqueous solution (40 g/L solution) of NaOH. The bars were

released from the molds at 24 hours of age, and immersed in 80 °C tap water for a period of 24 hours. After this time, the specimens were measured with a length comparator and immersed in the NaOH solution for 14 days. Additional measurements were made at 1, 5, 9, and 14 days after solution immersion.

3.3.3.5 Heat of Hydration

Heat of Hydration (HoH) was measured per ASTM C1702. A two-channel isothemal calorimeter (Calmetrix I-ca l 2000) was used for this study. An isothermal calorimeter operates at constant temperature of 77 °F and records heat energy needed to maintain this temperature for 7 days when a small concrete mixture sample (approx. 0.46 lbs) is placed. The sample was prepared using No. 7 sieve to screen out coarse aggregates.

4. EXPERIMENTAL RESULTS

This section presents a complete set of test results of 6 mixtures (out of 19 mixtures) containing MK product No. 1. However, the summary tables presented in this section include a placeholder for the remaining mixtures. The completed test results will be presented in the Phase-II report, as part of the RP 16-30 deliverables.

4.1 Fresh Properties

Table 12 shows the fresh concrete properties for all concrete mixtures. Slumps ranged from 1" to 10", and air contents typically ranged from 2.6%–5.5%.

4.2 Mechanical Properties

4.2.1 Compressive Strength

Table 13 shows compressive data at 1, 7, and 28 days of curing. The highest observed strengths were by the MK1-20 at 28-days of age, with an average strength of 3 specimens equaling 11,174 psi. This mixture also performed highest relative to the control mixture at any age—an increase of 44%. This MK product No. 1 showed a systematic increase in compressive strength up to 20% replacement for cement.

4.2.2 Tensile Strength

Table 14 shows split tensile strengths, MOR, and a ratio of the two for each mixture. As with compression, each average strength is accompanied by a percentage increase relative to the control.

Table 12 – Fresh concrete properties.

	Mixture Code	Slump (in)	Air Content(%)	Unit Weight (pcf)	Temperature (°F)
M1	Control	2.5	4.1%	146.4	73.4
M2	MK1-10	8.5	5.5%	157.8	75.7
M3	MK1-15	1.3	3.8%	144.4	73.4
M4	MK1-20	2.0	3.6%	143.4	66.6
M5	MK2-10	3.0	3.2%	144.6	84.3
M6	MK2-15	1.5	3.9%	149.8	59.7
M7	MK2-20	2.0	3.6%	144.8	75.2
M8	MK3-10	6.5	3.5%	144.4	78.1
M9	MK3-15	3.8	3.5%	144.0	78.8
M10	MK3-20	1.5	2.6%	144.2	84.6
M11	MK1-15_SLa-30	10.0	4.5%	140.6	76.0
M12	MK2-15_SLa-30	1.8	3.9%	141.4	73.9
M13	MK3-15_SLa-30	9.0	4.5%	136.4	75.6
M14	MK1-15_SLb-30	9.0	3.5%	144.6	83.7
M15	MK2-15_SLb-30	3.8	3.8%	143.6	88.2
M16	MK3-15_SLb-30	2.0	5.0%	144.8	80.1
M17	SLa-30	1.0	4.3%	136.8	68.2
M18	SLb-30	1.0	3.0%	146.8	82.4
M19	FA-45	6.0	0.0%	146.0	86.7

 $Table\ 13-Compressive\ strength\ (psi)\ for\ mixtures.$

Descrip	otion of Speci	mens	Compre	ssive Stren	ngth (psi)	% Increase Relative to Control			
Series	SCM Product(s)	Relpacement Level	2 ² C	7.Day 1.Day		94	285	Day	
Control	N.A.	N.A.	2138	-	5978	N.A.	7786	-	
		10%	2667	25%	6282	5%	9092	17%	
	MK1	15%	2926	37%	7858	31%	10070	29%	
		20%	2610	22%	8088	35%	11174	44%	
Binary		10%	~	~	~	~	~	~	
Replacements	MK2	15%	~	~	~	~	~	~	
by MK		20%	~	~	~	~	~	~	
		10%	~	~	~	~	~	~	
	MK3	15%	~	~	~	~	~	~	
		20%	~	~	~	~	~	~	
Dinon	SLa	30%	1038	-51%	5171	-13%	7657	-2%	
Binary Replacements	SLb	30%	~	~	~	~	~	~	
by Other SCMs	FA	45%	~	~	~	~	~	~	
	MK1 + SLa	15% + 30% =45%	1003	-53%	6341	6%	8570	10%	
	MK2 + SLa	15% + 30% =45%	~	~	~	~	~	~	
Ternary Replacements	MK3 + SLa	15% + 30% =45%	~	~	~	~	~	~	
by MK + Slag	MK1 + SLb	15% + 30% =45%	~	~	~	~	~	~	
	MK2 + SLb	15% + 30% =45%	~	~	~	~	~	~	
	MK3 + SLb	15% + 30% =45%	~	~	~	~	~	~	

[~] Denotes mixtures that are not a part of Phase 1, and are to be presented in the Phase-2 report.

 $Table\ 14-Tensile\ strength\ as\ both\ split-cylinder\ and\ MOR\ for\ concrete\ mixtures.$

Descrip	tion of Speci	mens	28-Day	0/ 1		0/ 1	
Series	SCM Product(s)	Relpacement Level	Split- Tension (psi)	% Increase Relative to Control	28-Day MOR (psi)	% Increase Relative to Control	SPT/MOR
Control	N.A.	N.A.	418	0%	711	0%	0.59
		10%	493	18%	640	-10%	0.77
	MK1	15%	544	30%	983	38%	0.55
		20%	476	14%	853	20%	0.56
Binary		10%	~	~	~	~	~
Replacements	MK2	15%	~	~	~	~	~
by MK		20%	~	~	~	~	~
		10%	~	~	~	~	~
	MK3	15%	~	~	~	~	~
		20%	~	~	~	~	~
Binary	SLa	30%	355	-15%	740	4%	0.48
Replacements by Other SCMs	SLb	30%	~	~	~	~	~
by Other Scivis	FA	45%	2	~	2	~	~
	MK1+SLa	15% + 30% =45%	423	1%	711	0%	0.59
	MK2 + SLa	15% + 30% =45%	~	~	2	~	~
Ternary	MK3+SLa	15% + 30% =45%	2	~	?	~	2
Replacements by MK + Slag	MK1+SLb	15% + 30% =45%	~	~	~	~	٧
	MK2 + SLb	15% + 30% =45%	~	~	~	~	~
	MK3+SLb	15% + 30% =45%	~	~	~	~	~

[~] Denotes mixtures that are not a part of Phase 1, and are to be presented in the Phase-2 report.

4.2.3 Modulus of Elasticity

Table 15 summarizes static and dynamic MOE (Es and Ed) results.

Table 15 – Modulus of elasticity (ksi).

Descript	ion of Specir	mens	20 D		20 D		
Series	SCM Product(s)	Relpaceme nt Level	28-Day Static MOE (ksi)	Increase Relative to Control	28-Day Dynamic MOE (ksi)	Increase Relative to Control	Es/Ed
Control	N.A.	N.A.	3886	0%	5438	0%	0.71
		10%	3628	-7%	5354	-2%	0.68
	MK1	15%	3686	-5%	5207	-4%	0.71
		20%	4087	5%	5246	-4%	0.78
Binary		10%	~	~	~	~	~
Replacements	MK2	15%	~	~	~	~	~
by MK		20%	~	~	~	~	~
		10%	~	~	~	~	~
	MK3	15%	~	~	~	~	~
		20%	~	~	~	~	~
Binary	SLa	30%	3959	2%	5586	3%	0.71
Replacements by Other SCMs	SLb	30%	~	~	~	~	~
by Other Scivis	FA	45%	~	~	~	~	~
	MK1+SLa	15% + 30% =45%	3668	-6%	4792	-12%	0.77
	MK2+SLa	15% + 30% =45%	~	~	~	~	~
Ternary	MK3+SLa	15% + 30% =45%	~	~	2	~	~
Replacements by MK + Slag	MK1+SLb	15% + 30% =45%	~	٠	~	٠	~
	MK2 + SLb	15% + 30% =45%	~	~	~	~	~
	MK3+SLb	15% + 30% =45%	2	~	2	~	~

[~] Denotes mixtures that are not a part of Phase 1, and are to be presented in the Phase-2 report.

4.2.4 Coefficient of Thermal Expansion

Table 16 contains CTE values for concrete mixtures. For all mixtures, the CTE increases relative to the control.

Table 16 - CTE values for concrete mixtures.

Descrip	otion of Speci	imens		
Series	SCM Product(s)	Relpacement Level	28-Day CTE (in/in/°F)	Increase Relative to Control
Control	N.A.	N.A.	5.35E-06	0%
		10%	5.53E-06	3%
	MK1	15%	5.96E-06	11%
Binary Replacements by MK		20%	5.66E-06	6%
		10%	~	~
	MK2	15%	~	~
		20%	~	~
		10%	~	~
	MK3	15%	~	~
		20%	~	~
Binary Replacements	SLa	30%	5.48E-06	2%
	SLb	30%	~	٧
by Other SCMs	FA	45%	~	~
	MK1+SLa	15% + 30% =45%	5.40E-06	1%
	MK2+SLa	15% + 30% =45%	~	~
Ternary	MK3+SLa	15% + 30% =45%	~	~
Replacements by MK + Slag	MK1+SLb	15% + 30% =45%	~	٠
	MK2 + SLb	15% + 30% =45%	~	~
	MK3 + SLb	15% + 30% =45%	~	~

[~] Denotes mixtures that are not a part of Phase 1, and are to be presented in the Phase-2 report.

4.3 Durability Properties

4.3.1 Drying Shrinkage

Table 17 shows the progression of drying shrinkage for concrete mixtures. At an age of 140 days after casting, MK1-15 demonstrated 22% less shrinkage than the control mixture. In descending order (most to least), MK product No. 1 binary mixtures ranked as follows: MK1-10, MK1-20, and MK1-15. At 140 days after casting, binary product 'a' slag demonstrated the most shrinkage.

Table 17 – Drying shrinkage of concrete mixtures.

Descripti	Description of Specimens		28-Day Increase								
Series	SCM Product(s)	Relpacement Level	Curing Expansion	From Control	32-Days	35-Days	42-Days	56-Days	84-Days	140-Days	252-Days
Control	N.A.	N.A.	0.015%	0%	0.012%	0.008%	-0.007%	-0.010%	-0.020%	-0.021%	~
		10%	0.032%	109%	0.024%	0.014%	0.007%	0.000%	-0.006%	-0.008%	~
	MK1	15%	0.039%	154%	0.025%	0.018%	0.012%	0.004%	0.000%	0.001%	~
		20%	0.032%	107%	0.023%	0.019%	0.001%	-0.007%	-0.008%	-0.006%	~
Binary		10%	~	~	~	~	~	~	~	~	~
Replacements by	MK2	15%	2	~	~	~	~	~	~	~	~
MK		20%	~	~	~	~	~	~	~	~	~
		10%	~	~	~	~	~	~	~	~	~
	MK3	15%	~	~	~	~	~	~	~	~	~
		20%	~	~	~	~	~	~	~	~	~
Binary	SLa	30%	0.008%	-46%	0.002%	-0.005%	-0.013%	-0.020%	-0.029%	-0.027%	~
Replacements by Other SCMs	SLb	30%	~	~	~	~	~	~	~	~	~
Other Scivis	FA	45%	~	~	~	~	~	~	~	~	~
	MK1 + SLa	15% + 30% =45%	0.023%	48%	0.019%	0.012%	0.002%	-0.004%	-0.010%	-0.004%	~
	MK2 + SLa	15% + 30% =45%	~	~	~	~	~	~	~	~	~
Ternary	MK3 + SLa	15% + 30% =45%	~	~	~	~	~	~	~	~	~
Replacements by MK + Slag	MK1 + SLb	15% + 30% =45%	~	~	~	~	~	~	~	~	~
	MK2 + SLb	15% + 30% =45%	~	~	~	~	~	~	~	~	~
	MK3 + SLb	15% + 30% =45%	~	~	~	~	~	~	~	~	~

[~] Denotes mixtures that are not a part of Phase 1, and are to be presented in the Phase-2 report.

4.3.2 Rapid Chloride-Ion Permeability Test

RCPT results for concrete mixtures appear in Table 18. At all levels, binary replacements of cement by MK reduce the permeability by two classes from the control. Binary slag mixture for product 'a' performed similarly to the control. Ternary mixtures saw reductions in permeability comparable to those of binary MK replacements, with a notable low for MK3-15_SLa-30.

Table 18 – RCPT results for concrete mixtures.

Desc	ription of Specin	nens	28-Day RCPT			
Series	SCM Product(s)	Relpacement Level	(Cumulative Coulombs Passed)	% Increase Relative to Control	Permeability Classification	
Control	N.A.	N.A.	2776	0%	Moderate	
		10%	914	-67%	Very Low	
	MK1	15%	588	-79%	Very Low	
		20%	984	-65%	Very Low	
Binary		10%	~	~ ~		
Replacements	MK2	15%	~	~	~	
by MK		20%	~	~	~	
		10%	~	~	~	
	MK3	15%	~	~	~	
		20%	2	~	~	
Binary Replacements by Other SCMs	SLa	30%	2876	4%	Moderate	
	SLb	30%	~	~	~	
	FA	45%	~	~	~	
Ternary Replacements by MK + Slag	MK1 + SLa	15% + 30% =45%	711	-74%	Very Low	
	MK2 + SLa	15% + 30% =45%	~	~	~	
	MK3 + SLa	15% + 30% =45%	2	~	٧	
	MK1 + SLb	15% + 30% =45%	~	~	~	
	MK2 + SLb	15% + 30% =45%	~	~	~	
	MK3 + SLb	15% + 30% =45%	~	~	~	
	-					

[~] Denotes mixtures that are not a part of Phase 1, and are to be presented in the Phase-2 report.

4.3.3 Resistance to Sulfate Attack

Table 19 shows sulfate expansion data. All mixtures performed similarly to each other at 91 days of exposure to sulfate solution except for the control, which showed approximately 0.04% more expansion.

Table 19 – Percent sulfate expansion.

Description of Specimens										
Sarias	SCM	Relpacement	0-Day	7-Day	14-Day	21-Day	28-Day	56-Day	91-Day	105-Day
	Product(s)	Level								
Control	N.A.	N.A.	0.000%	0.008%	0.013%	0.017%	0.021%	0.040%	0.080%	0.115%
Binary Replacements by MK	MK1	10%	0.000%	0.008%	0.014%	0.016%	0.019%	0.026%	0.040%	0.051%
		15%	0.000%	0.011%	0.018%	0.021%	0.024%	0.033%	0.046%	0.056%
		20%	0.000%	0.011%	0.016%	0.018%	0.021%	0.029%	0.045%	0.054%
	MK2	10%	0.000%	~	~	~	~	~	~	~
		15%	0.000%	~	~	~	~	~	~	~
		20%	0.000%	~	~	~	~	~	~	~
	MK3	10%	0.000%	~	~	~	~	~	~	~
		15%	0.000%	~	~	~	~	~	~	~
		20%	0.000%	~	~	~	~	~	~	~
Binary Replacements by Other SCMs	SLa	30%	0.000%	0.011%	0.018%	0.027%	0.037%	0.129%	0.507%	0.822%
	SLb	30%	0.000%	~	~	2	2	2	~	~
	FA	45%	0.000%	~	~	?	?	~	2	~
Ternary Replacements by MK + Slag	MK1+SLa	15% + 30% =45%	0.000%	0.011%	0.016%	0.019%	0.021%	0.030%	0.046%	0.056%
	MK2 + SLa	15% + 30% =45%	0.000%	~	~	~	~	~	~	~
	MK3 + SLa	15% + 30% =45%	0.000%	~	~	~	~	~	~	~
	MK1+SLb	15% + 30% =45%	0.000%	~	~	~	~	~	~	~
	MK2 + SLb	15% + 30% =45%	0.000%	~	~	~	~	~	~	~
	MK3 + SLb	15% + 30% =45%	0.000%	~	~	~	2	~	~	~

~ Denotes mixtures that are not a part of Phase 1, and are to be presented in the Phase-2 report.

4.3.4 Resistance to Alkali-Silica Reaction

Table 20 includes the percentage expansion obtained from ASR tests.

Table 20 – Percent expansion from ASR results.

Description of Specimens							
Cowing	SCM Relpacement		1-Day	5-Days	9-Days	14-Days	
Series	Product(s)	Level					
Control	N.A.	N.A.	0.000%	0.031%	0.086%	0.141%	
		10%	0.001%	0.012%	0.031%	0.049%	
Binary	MK1	15%	0.002%	0.007%	0.020%	0.033%	
		20%	0.003%	0.002%	0.017%	0.033%	
	MK2	10%	~	~	~	~	
Replacements		15%	2	2	2	~	
by MK		20%	2	2	2	~	
	MK3	10%	~	~	~	~	
		15%	2	2	2	~	
		20%	?	?	~	~	
Binary Replacements by Other SCMs	SLa	30%	0.002%	0.015%	0.066%	0.117%	
	SLb	30%	2	2	~	~	
	FA (class F)	45%	2	2	~	~	
Ternary Replacements by MK + Slag	MK1+SLa	15% + 30% =45%	0.000%	0.001%	0.018%	0.034%	
	MK2 + SLa	15% + 30% =45%	~	~	~	~	
	MK3 + SLa	15% + 30% =45%	~	~	~	~	
	MK1+SLb	15% + 30% =45%	~	~	~	~	
	MK2 + SLb	15% + 30% =45%	~	~	~	~	
	MK3 + SLb	15% + 30% =45%	~	~	~	~	

[~] Denotes mixtures that are not a part of Phase 1, and are to be presented in the Phase-2 report.

4.3.5 Heat of Hydration

Figures 22 and 23 include the power and energy curves from the calorimeter test described in Section 3.3.3.5. Either specimen MK1-15_SLa3 or MK15 + SL30 (product 'a') is most promising in terms of HoH reduction. In this section, additional mixtures including slag product 'b' and fly ash are presented for comparison.

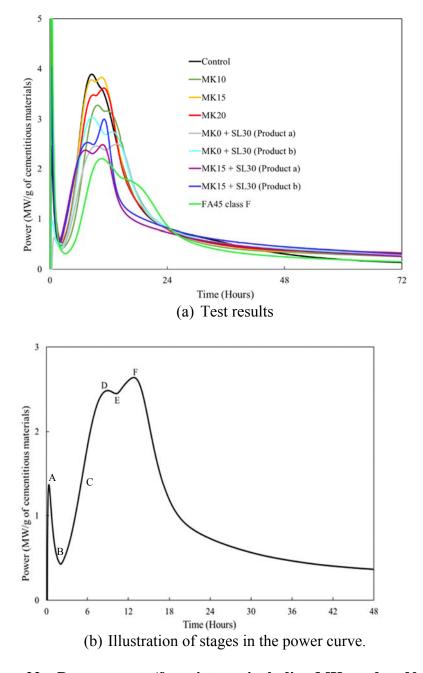


Figure 22 – Power curves (for mixtures including MK product No. 1).

An I-Cal HPC Isothermal calorimeter per ASTM C1702 (HoH testing) and ASTM C1679 (isothermal calorimetry) was used to measure the heat generated from the concrete mixtures. In this method, any heat produced during hydration is removed from the system, and the temperature around the sample is maintained constant. The heat generated by the cement hydration reaction is measured by precision heat flow sensors in a form of electrical power (voltage). The shape of the thermal power curve reflects the hydration process of the cement or cementitious sample. The integration of the thermal power curve over time produces energy or the heat of hydration (see Figure 23), which is generally correlated to the compressive strength of the mix. The calorimeter measures the rate of cementitious material hydration which in turn determines the rate of set and strength development. The hydration process of cement is generally divided into a number of stages (ASTM C1679-08) shown in Figure 22(b):

- A. Rapid initial thermal power or a strong initial exotherm which is caused by rapid dissolution and initial hydration of mainly the aluminate phase.
- B. Dormant period in which the hydration rate rapidly decreases as aluminate reacts with calcium and sulfate to form ettringite-like phases.
- C. Acceleration period which is the initiation of the strength-generating alite or silicate hydration. This results in a broad exotherm. Time to set normally occurs early in this stage.
- D. Sulfate depletion when the mixture runs out of sulfate in the pore solution due to the ongoing alite and aluminate hydration.
- E. and F. These two stages are generally characterized by the type and amount of pozzolans used in a mixture.

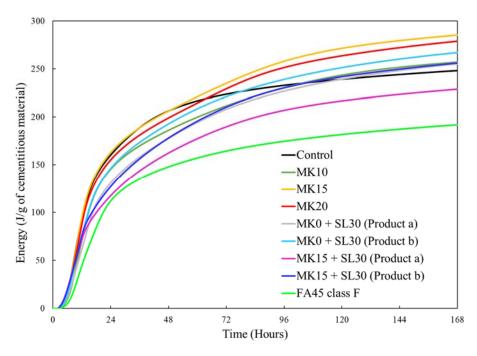


Figure 23 – HoH (for mixtures including MK product No. 1).

5. ANAYSIS OF TESTING RESULTS

5.1 Introduction

This section includes the discussion and analysis of all concrete mixtures including binary and ternary cement replacements with MK product No. 1 (MetaMax) and/or slag product 'a' (Argos's Grade 120). The overall analysis of results from MK product No. 2 (PowerPozz), product No. 3 (Kaorock), and slag product 'b' (Lehigh Cape Slag) will be presented in the Phase-II or RP 16-30 report.

The six mixtures include the following: a 10%, 15%, or 20% percent replacement of cement with MK product No. 1 (MK1-10, MK1-15, MK1-20), a 30% replacement by slag product 'a' (SLa-30 and SLb-30), a 45% replacement with combined MK and slag products ('MK1-15 SLa-30' and 'MK1-15 SLb-30'), and the control mixture.

5.2 Evaluation of Metakaolin Product No. 1

The replacement of cement by MK product No. 1 led to concrete mixtures with considerably higher strengths, lower drying shrinkage, and higher durability.

5.2.1 Mechanical Properties

Compressive strengths were higher than the control at all ages and for all replacement levels (10%, 15%, and 20%). When compressive data are presented by percentage increase from the control, it can be seen that product No. 1 binary mixtures display higher strength increases than is common in the literature (Saravanan, 2015; Paiva, 2012). Typical increases in strength range from 10% to 30%, while MK1-20 was 44% stronger than the control at 28 days of curing. A few studies have reported similar increases in strength (e.g., Fitos, 2015). In addition, the optimum replacement level with respect to compression for product No. 1 was higher than other MKs in the literature with similar water-to-cement ratios and high SiO₂+Al₂O₃+Fe₂O₃ contents. Compressive strength continued to increase at all ages up to 20% replacement of cement by product No. 1. Compressive strength plots are shown in Figure 24.

5.2.1.1 Compressive Strength

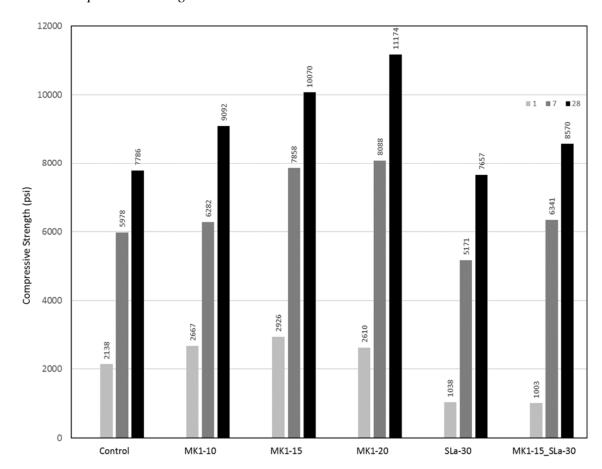


Figure 24 – Compressive data for mixtures belonging to the product No. 1 series.

The 1-day strengths of product No. 1 binary MK concrete mixtures were an average of 28% higher than control mixtures. As the pozzolanic reaction does not take place at this early age, these results support the notion that fine MK particles help densify concrete at early ages via particle packing. Other findings from Figure 24 are as follows:

- All mixtures including MK binary mixtures had higher 1-day, 7-day, and 28-day strengths (increase of 600 psi, 1430 psi, and 2330 psi, respectively).
- Mixture rankings based on 28-day strengths are as follows:
 MK1-20 > MK1-15 > MK1-10 > MK1-15 SLa-30 > Control.

- MK1-20 (or 20% cement replacement by MK) showed the highest strength in the series (increase of 3,388 psi or 43.51% from the control).
- Strength increases near or above 5,000 psi occurred for MK1-15, MK1-20, and MK1-15_SLa-30 mixtures between 1 and 7 days.
- SLa-30 and MK1-15_SLa-30 performed similarly to the control, with the note that 1-day strengths for these mixtures were lower—just above 1,000 psi.

5.2.1.2 Tensile Strength

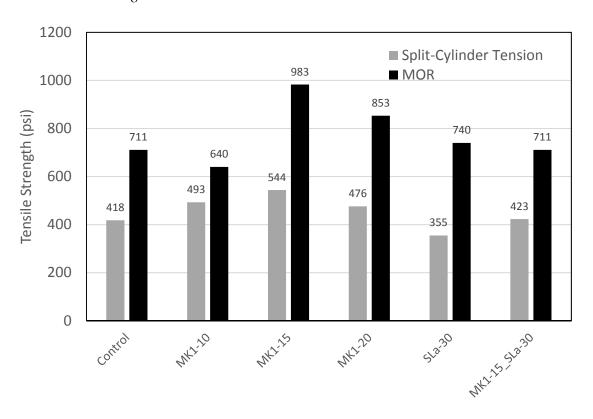


Figure 25 – Tensile strengths: split-cylinder and MOR for mixtures including MK product No. 1.

Tensile strength results follow nearly the same trend as the compressive data. With the exception of MK1-10 MOR values, tensile strengths in general increased 14%–38% from the control. MK1-15 attained the highest 28-day strengths for both split-tension and MOR. Other findings from Figure 25 are as follows:

- All mixtures showed increased strengths from control mixtures, with the exception of MK1-10's MOR results.
- High for both MOR and split-cylinder tests was MK1-15, with an increase of 272 psi (38%) and 126 psi (30%), respectively.

5.2.1.3 Coefficient of Thermal Expansion

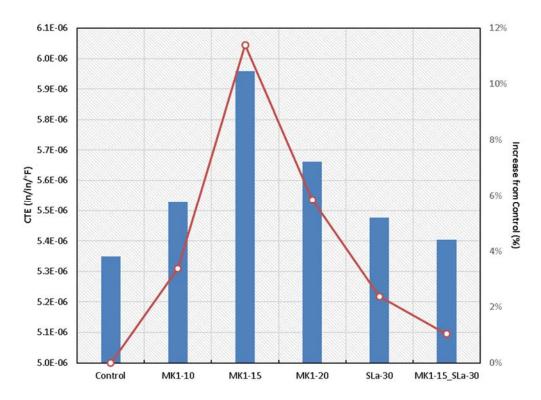


Figure 26 – CTE results for series product No. 1.

Figure 26 presents the CTE test results. CTE values are ordered lowest to highest as follows: Control > MK1-15 SLa-30 > SLa-30 > MK1-10 > MK1-20 > MK1-15.

5.2.1.4 Modulus of Elasticity

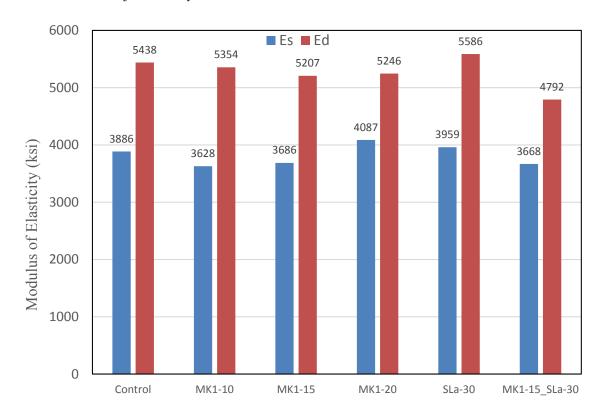


Figure 27 – Static and dynamic Young's moduli (Es and Ed) for product No. 1 series.

Figure 27 includes the MOE values determined from static and dynamic tests:

- Only SLa-30 showed a higher dynamic modulus than the control.
- Only MK1-20 and SLa-30 showed a higher static modulus than the control.

5.2.2 Durability Properties

5.2.2.1 Dry Shrinkage

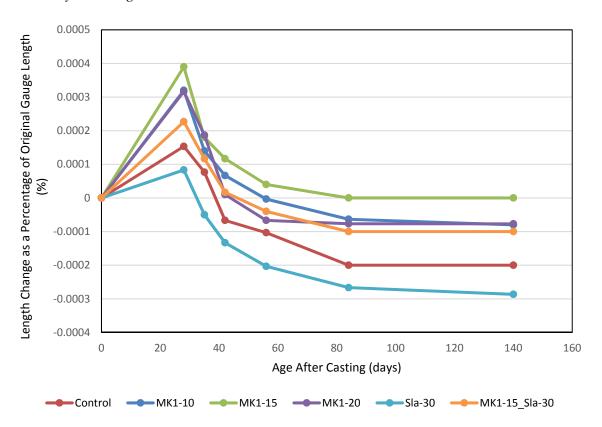


Figure 28 – Drying shrinkage for product No. 1 series up to 140 days of age.

Figure 28 illustrates the product No. 1 results. The main findings are summarized below:

- Mixtures incorporating MK showed greatly reduced drying shrinkage.
- The best performing mixture was MK1-15, which showed high expansion during the first 28 days (curing period).
- A reduced shrinkage rate between 56 and 84 days of age is a good indicator of shrinkage slowing.

5.2.2.2 Rapid Chloride Penetration

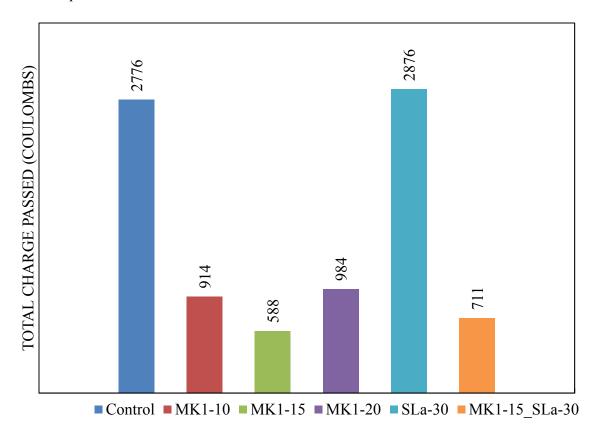


Figure 29 – Total charge (C) passed during ASTM C1202 for product No. 1 series.

Figure 29 indicates the most influential factor affecting total charge passed is the inclusion of MK. Therefore, all mixtures containing MK belong to permeability class "Very Low" per ASTM C1202. The top performing mixture was MK1-15.

5.2.2.3 Sulfate Expansion

The control mixture exceeded the 6-month expansion limit of 0.10% by 15 weeks in solution. All other mixtures (mixtures including MK) were comparable to each other.

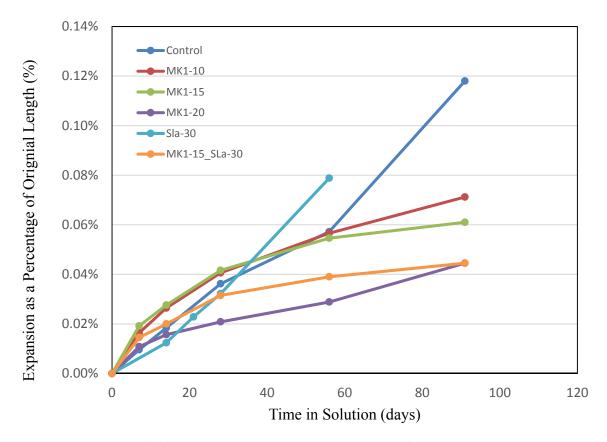


Figure 30 – Sulfate expansion up to 91 days of age for product No. 1 series.

5.2.2.4 Alkali-Silica Reaction Expansion

The inclusion of MK greatly reduces expansion of mortar bars in Na(OH) solution. Additional benefits of a binary replacement of cement diminish after 15% MK. Ternary mixture performs similarly to 15% and 20% MK mixtures.

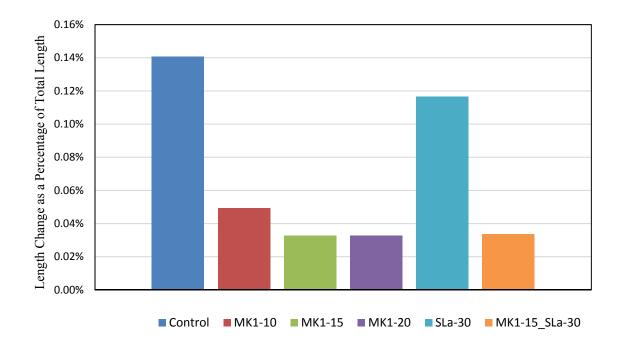


Figure 31 – Final ASR expansions for product No. 1 series.

5.2.2.5 Heat of Hydration

Figures 32 and 33 present a comparison of compressive strength and HoH. Two notable mixtures—MK0+SL30 and MK15+SL30 (product 'a')—reduce HoH while providing superior strength development when compared to the control mixture.

- HoH reduction by 30% cement replacement with slag (product 'a'):
 Relative to the control mixture, HoH is reduced within the first 24 hours due to the 30% replacement of cement with slag. The HoH slowly increases due to the pozzolanic reaction, although the seven-day data indicates that the total energy is comparable to the control case.
- HoH reduction by 45% cement replacement with combined 30% slag (product 'a') and 15% MK (No. 1):

The HoH was reduced by the 45% cement replacement within 24 hours. Furthermore, HoH slowly increases between three and seven days due to the pozzolanic reaction of the MK product (No. 1). Overall, HoH is reduced by 10% in the ternary mixture, whereas it is reduced by 25% when 45% of the Portland cement was replaced with the fly ash (Class F) product.

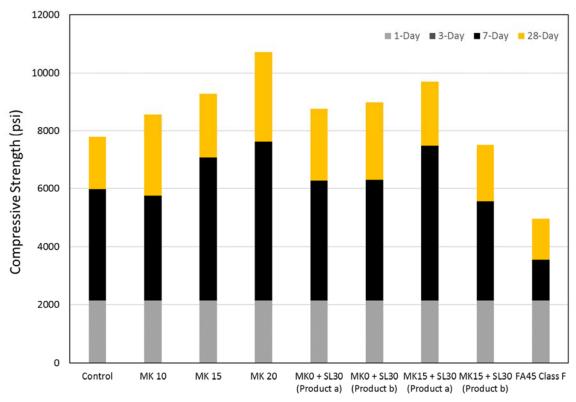


Figure 32 – Compressive strength for increasing cement replacement levels.

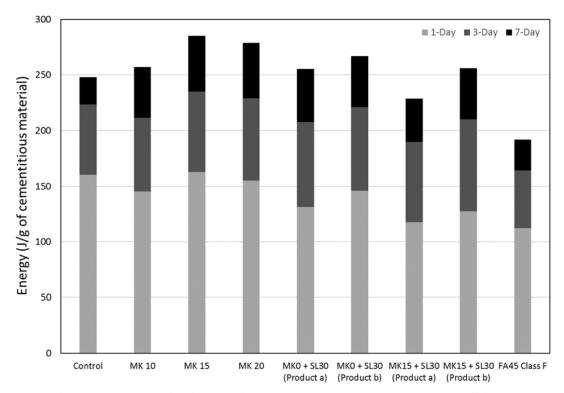


Figure 33 – HoH for increasing cement replacement levels by SCMs.

For the ternary mixtures including slag product 'a', HoH is significantly reduced. This finding may be attributed to the relatively slower strength development of slag product 'a' as well as the material fineness. The Blaine fineness of slag product 'b' is greater than that of slag product 'a' (see Table 9), and the alumina content in slag product 'a' is slightly higher. For the ternary mixture including slag product 'b', HoH is higher than that of the control mixture.

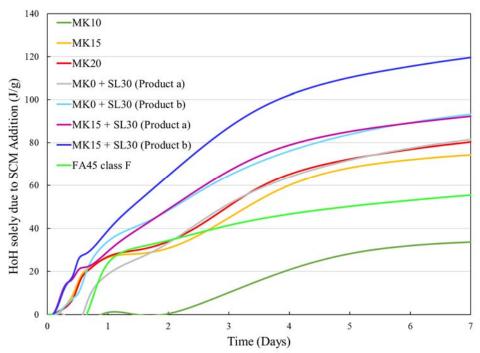


Figure 34 – Predicted HoH solely due to SCMs (or pozzolanic reactions) including MK product No. 1.

Figure 34 is developed by subtracting the total energy of each mixture from the total energy obtained from the control mixture (refer to Figure 23). A linear extrapolation of cement hydration energy is considered. The slope (rate) of energy produced by pozzolans is noteworthy in this figure, especially compared to the slope for the mixture including fly ash (FA45 Class F). Slag product 'a' shows a reduction in HoH compared to the Class F fly ash between 24 and 48 hours.

5.3 Evaluation of Binary and Ternary SCMs

Table 21 provides a summary of mechanical and durability properties obtained from concrete mixtures containing MK. In addition, the following findings are summarized:

- The binary replacements of cement with MK significantly enhance both mechanical and durability properties. At the same time, fine materials have a higher water demand and thus reduce the workability of concrete.
- The ternary replacements of cement with combined slag and MK significantly reduce HoH and enhance the durability properties; thus, they could possibly alleviate the thermal cracking potential of concrete.

Table 21 – Summary of findings for MK mixtures.

Property	Literature Review	Product No. 1 Findings
		(from this study)
Workability	Decrease	Decrease
Setting Time	Increase	Increase
Compressive Strength	Increase	Increase
Tensile Strength	Increase	Increase
Modulus of Elasticity	Increase	Increase
Alkali-Silica Reactivity	Decrease	Decrease
Permeability	Decrease	Decrease
(Cl ⁻ , water, gas, etc.)		
Shrinkage	Decrease	Decrease
Sulfate Resistance	Increase	Increase
	Decrease	Varies
Heat of Hydration	/Increase	(Increase with a 15%
		replacement; slightly
		decrease with a 10% MK
		replacement within the first
		3 days of placement)

6. CONCLUSIONS

6.1 Binary Replacements of Cement with Metakaolin Products

Based on the findings of MK product No. 1 presented herein, the following conclusions are made:

- 1. Optimum replacement limit is approximately 15%.
- 2. Workability reduces due to the fine material, despite the use of PCE-based admixtures.
- 3. Mechanical properties, including compressive, tensile, and flexural strength, enhance with the optimum replacement level of MK.
- 4. CTE values increase with increasing mechanical strengths and decreasing permeability.
- 5. Durability properties, including ASR/sulfate resistance and shrinkage, significantly enhance with the optimum replacement level of MK. Overall, the durability tests show drastic improvements in concrete quality with nearly any level of MK replacement of cement.

6.2 Binary Replacements of Cement with Slag Products

Based on the findings of the two slag products presented herein, the following conclusions are made:

- 1. The sulfate expansion increases in the binary mixtures including slag product 'a'.
- 2. The chloride permeability is lower in the control specimen based on the 28th day test although the permeability in the binary specimens is expected to decrease when a RCPT is conducted 3 months after concrete placement.

6.3 Ternary Replacements of Cement with Combined Metakaolin Products and Slag Products

Based on the findings of the ternary mixtures, the following conclusions are made:

- 1. Ternary mixtures reduce HoH while not compromising strength development.
- 2. They significantly enhance the durability (e.g., reduced RCP, shrinkage, ASR and enhanced sulfate resistance) of concrete mixtures.
- 3. The workability of concrete mixtures reduces, requiring increased dosage of admixtures.

Other conclusions are pending the conclusion of Phase II work.

7. RECOMMENDATIONS

Based on this evaluation of MK and blast furnace slag products as binary and ternary replacements of cement, it is highly recommended that GDOT consider other supplementary materials (e.g., silica fume and ground calcium carbonate), as well as increased cement replacement levels with SCMs. Furthermore, it should be recognized that SCMs play a very important role in the durability enhancement of concrete.

The following specific recommendations are provided:

- Each MK product has a unique chemical composition, fineness, and kaolin purity; thus, each product should be evaluated for its performance, durability, and application.
- Optimum cement replacement levels with MK vary among products, although a 10%-15% replacement, as of the end of Phase I, appears to be representative of MK products sourced from Georgia and South Carolina.
- The mechanical properties of binary mixtures including slag products could significantly vary among products. Strength development is directly correlated with HoH in concrete; therefore, thermal cracking potential must be studied before a cement replacement level with slag is recommended for mass concrete mixtures.
- The HoH in ternary mixtures (i.e., a 45% cement replacement) is significantly reduced without considerably compromising the mechanical properties of concrete. Increased cement replacement levels and other ternary replacements (e.g., silica fume and slag) of cement are highly recommended, particularly for mass concrete mixtures.

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