COMPARISON OF COMMERCIALLY-AVAILABLE METAKAOLINS AND SLAGS IN BINARY AND TERNARY CONCRETE MIXTURES

by

MATTHEW SEAN SULLIVAN

(Under the Direction of Mi G. Chorzepa)

ABSTRACT

The use of metakaolin (MK) as a supplementary cementitious material (SCM) has been documented in the literature for over 20 years. However, few studies have compared the performance of multiple commercially-available MKs as both binary and ternary replacements of cement. A total of 18 cement-pozzolan combinations were evaluated; nine binary MK combinations, three binary combinations incorporating other pozzolans, and six ternary combinations of MKs and slags. The mixture parameters were: cement content of 711 pcy, a coarse aggregate content of 1,660 pcy, and a w/cm ratio of 0.43. Tests measured compressive strength, flexural strength, split-cylinder tensile strength, dynamic modulus of elasticity, drying shrinkage, coefficient of thermal expansion, resistance to chloride-ion penetration, and resistance to sulfate attack and alkali-silica reaction (ASR). Two of three MKs consistently contributed to increased mechanical strengths, higher indicators of durability, reduced drying shrinkage, and higher CTE values. Recommendations for use are discussed.

INDEX WORDS: Metakaolin, blast furnace slag, ternary, strength, durability, concrete, SCM, pozzolan, mineral admixtures, CTE

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CHAPTER 1

INTRODUCTION

This chapter will serve the purpose of introducing metakaolin as a material, as well as its usage as a SCM in concrete. Gaps in current MK literature will be discussed as they pertain to the research objectives of this study.

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 MK. MK, 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 about 1 to 2 micrometers [1].

When MK is used as a partial cement replacement, improved performance has been observed such as increased strength and reduced permeability [2]. Marikunte and Phelps (2012) statistically demonstrated that MK contributed more to concrete achieving high performance than reducing water content. San Nicolas et al. (2014) concluded that the substitution by MK (25% by weight) improves the durability of concrete [3]. Ferreira et al. (2015) reported improved strength, durability properties and chloride penetration resistance of concrete with MK [4].

Khatib et al. (2009) found that the use of MK when used with fly ash (FA) as a cement replacement reduced concrete shrinkage [5]. Lagier and Kurtis (2007) found that the use of MK accelerated the hydration process as a result of its higher surface area [6]. However, Brykov et al. (2015) finds that it depends on the MK dosage [7]. Furthermore, highly reactive MK is widely used for concrete overlay design by Illinois, Iowa, and a few other state departments of transportation (DOT) due to its enhanced durability. Research has documented positive responses, as listed below, when using MK in concrete mixtures; however, no comprehensive study today has examined its use in binary and ternary mixtures and established appropriate limits for its usage.

Advantages of using MK as a partial cement replacement:

- Increased compressive and flexural strengths
- Increased resistance to chemical attack and durability
- Enhanced workability
- Improved color by lightening the color of concrete
- 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 either ASTM (American Society for Testing and Materials) C168 or AASHTO (American Association of State and Highway Transportation Officials) M321 for MK for use in hydraulic cement. The Illinois DOT provides a special provision which includes alkali-silica reaction mitigation requirements where the average alkali content ($Na_2O + 0.658K_2O$) of high reactivity MK must be less than 1.0%. In addition, the content of Silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3) must exceed 80%. The Texas DOT provides 85% requirement for the same chemical composition (DMS-4635, 2014). 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 MK to 10% of portland cement by weight, whereas use of FA 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 the portland cement on a pound for pound basis in all concrete. The California DOT recommends that MK is used in dosages ranging from 5%-10%, by mass of the cementitious material. The Montana DOT allows up to 20% by weight of the total cementitious material. Ramezanianpour & Jovein (2012) recommended that the optimum replacement of MK be 12.5% and 10% at water-to-cement ratio of 0.4 and 0.35, respectively [8]. In Nebraska, the maximum pozzolanic content should not exceed 15-25% of the total cementitious material. Wisconsin requires that MK must be from an approved supplier on the department's approved product list. Furthermore, the supplier must have an in-place quality management program, where daily testing is performed to determine uniformity.

Current Georgia Department of Transportation (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 specifies that slag may comprise no more than 75% by mass of total cementitious and pozzolanic materials. Class F FA 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 FA and slag in the state, it is possible to consider supplementary cementitious materials such as MK to control heat of hydration. There is however some disagreement among past studies on the effect of microsilica (or MK) on the heat of hydration.

While in some studies, the replacement of cement by 10% and 20% microsilica slightly reduced early heat of hydration [9]; other studies showed otherwise [10]. However, the physical characteristics and chemical composition of MK play an important factor on the effect of heat of hydration. Alshamsi (1997) limited the cement replacement to 10%, and the chemical composition of MK differs from what is available in today's market. Therefore, it is necessary to evaluate the feasibility of using MK products available in the Georgia market to reduce the heat of hydration in mass concrete elements. In a recent study, increased MK replacement (from 10% to 14%) minimized the total heat evolved, although 10% was found optimal with the consideration of mechanical properties [11].

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 MK and other supplementary materials as a partial replacement of cement. Furthermore, it is important to determine whether and how MK should be specified.

Problem Statement

There is a tangible risk of the coal market being unable to sustain the current volume of FA usage in U.S. concretes. FA is an all-important SCM used in mitigating deleterious cracking due to the large thermal gradients in mass concrete. It is therefore important to evaluate alternative SCMs to maintain the market habits of the ready-mix industry. MK in a locally-available option for the state of Georgia. Furthermore, several state DOTs have adopted and specified commercial MKs for use in concrete. Despite Georgia being a world-leading kaolin producer, the use of MK has yet to be specified in the GDOT's standard specifications.

The USGS estimates that nearly 8.5 million metric tons of kaolin are mined from Georgia each year [12]. It 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 [13]. Therefore, MK is not a byproduct of another process. FA, silica fume (SF), and blast furnace slag are all secondary materials. Placements of mass concrete demand considerable control of temperature rise due to the heat of hydration of cementitious materials. Typical temperature rise in concrete mixtures range between 80°F and 100°F. ACI recommends the placement temperature of 58°F below for the 100°F temperature rise concrete; however, it is particularly challenging to meet this temperature requirement in Georgia. Generally, the temperature rise at concrete placements can be reduced to 70°F with a large percentage of portland cement replaced with Class F FA or slag. However, there has been a shortage of FA and slag. Therefore, Class F FA and slag must be replaced 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 stresses at the surface. Once the maximum temperature in the interior exceeded the accepted threshold value, DEF (delayed ettringite formation) can occur in mass concrete elements. Therefore, DEF can be prevented by limiting the internal concrete temperature during its very early life. The maximum temperature suggested by prior research efforts to prevent DEF in concrete elements is 160°F. This reduced temperature can be achieved by direct specification of temperature allowable, by limiting the cement content, or by specifying the use of low heat supplementary cement materials.

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

Objective

This research study aims to find natural, lightly processed, and economical alternatives to FA that perform similarly to Class F FA 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. MK is a naturally-occurring pozzolan and is included as an ASTM C618 Class N Pozzolan. As a pozzolan, MK would provide similar improved concrete performance in the form of 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 the 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 MK to be used in mixtures and the subsequent concrete performance. Appropriate usage of MK in both binary and ternary concrete mixtures will provided, along with preliminary specifications for its usage in DOT concrete.

Research Significance

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

CHAPTER 2

LITERATURE REVIEW

Overview

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 the cement. During the production of cement clinker, $CaCO_3$ (calcium carbonate) is converted into calcium oxide via calcination inside a rotary kiln [14]. The second product, CO_2 (carbon dioxide), is then emitted or retained. A simplified chemical equation is given as Eq. (1).

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2 \qquad \text{(Eq. 1)}$$

The Intergovernmental Panel on Climate Change (IPCC) states that the cement production is the largest emitter of CO_2 in the industrial sector [15]. Worldwide, it is estimated that for every ton of cement produced approximately 0.82 tons of carbon dioxide are released into the atmosphere [16]. The significance is that approximately 5% of the world's anthropogenic carbon emissions can be traced to the production of cement [17]. However, it is because it is both financially and environmentally costly that reducing the proportion of cement in concrete mixtures has gained and kept popularity for decades. To this end, SCMs 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 possible ways:

- Reduce costs
- Improve fresh and hardened properties of concrete
- Reduce environmental impact
- Reuse waste materials
- Enhance aesthetics

A SCM is any material that, when used conjointly with cement, chemically reacts with the 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, a brief chemical description is given as Eq. 2.

$$S + CH + H \rightarrow C\text{-}S\text{-}H \qquad \text{(Eq. 2)}$$

According to the portland Cement Association (PCA) SCMs are used in at least of 60% of all ready mixed concrete [1]. The three most commonly used SCMs are FA, blast furnace slag, and SF. As a result, these are historically the SCMs that were adopted and specified for use by U.S. state DOTs In recent years however, several state DOTs have allowed for the use of a calcined clay called MK.

MK is an aluminous and siliceous natural pozzolan that conforms to ASTM C618, 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, $Al_2Si_2O_5(OH)_4$ [18]. 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. It is one of the most recently implemented SCMs [19], and differs from most other SCMs in that it is a primary product. This allows for strict quality standards, and therefore provides an option for consistent, high-performance concrete.

Manufacturing and Processing

Kaolin is rigidly structured. Before activation, kaolin consists of alternating sheets of tetrahedral silica (SiO_4) and octahedral alumina (AlO_6) 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) [20]. Kaolin can be thermally or mechanically activated, although it is much more prevalent that it is thermally activated [21]. The activation is perfect if all hydroxyl groups binding the alumina and silica sheets in the kaolin are broken. This dehydroxylation results in a disorganized, non-crystalline structure that is highly reactive. This amorphous nature of the MK is the source of its reactivity.

$$OH + OH \leftrightharpoons H_2O\uparrow + O \qquad \text{(Eq. 3)}$$

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 the literature and found that the optimum range of temperatures was in the ballpark of 600-850°C [22]. The optimum calcining time varied by temperature, however 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 [23]. This indicates that a slower rate of calcination is preferable so long as the temperature is appropriate. The significance of the method of calcining is 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 (SiO_2), spinel ($2Al_2O_3 \cdot 3SiO_2$), and mullite ($2[3Al_2O_3 \cdot 2SiO_2]$) [18]. A successful activation hits the sweet spot in-between.

Fitos et al. [21] 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 it was found that 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.

Physical and Chemical Characteristics

The general formula for MK is $Al_2O_3 \cdot 2SiO_2$ and is typically characterized in the literature by two properties: material fineness, and composition by oxides.

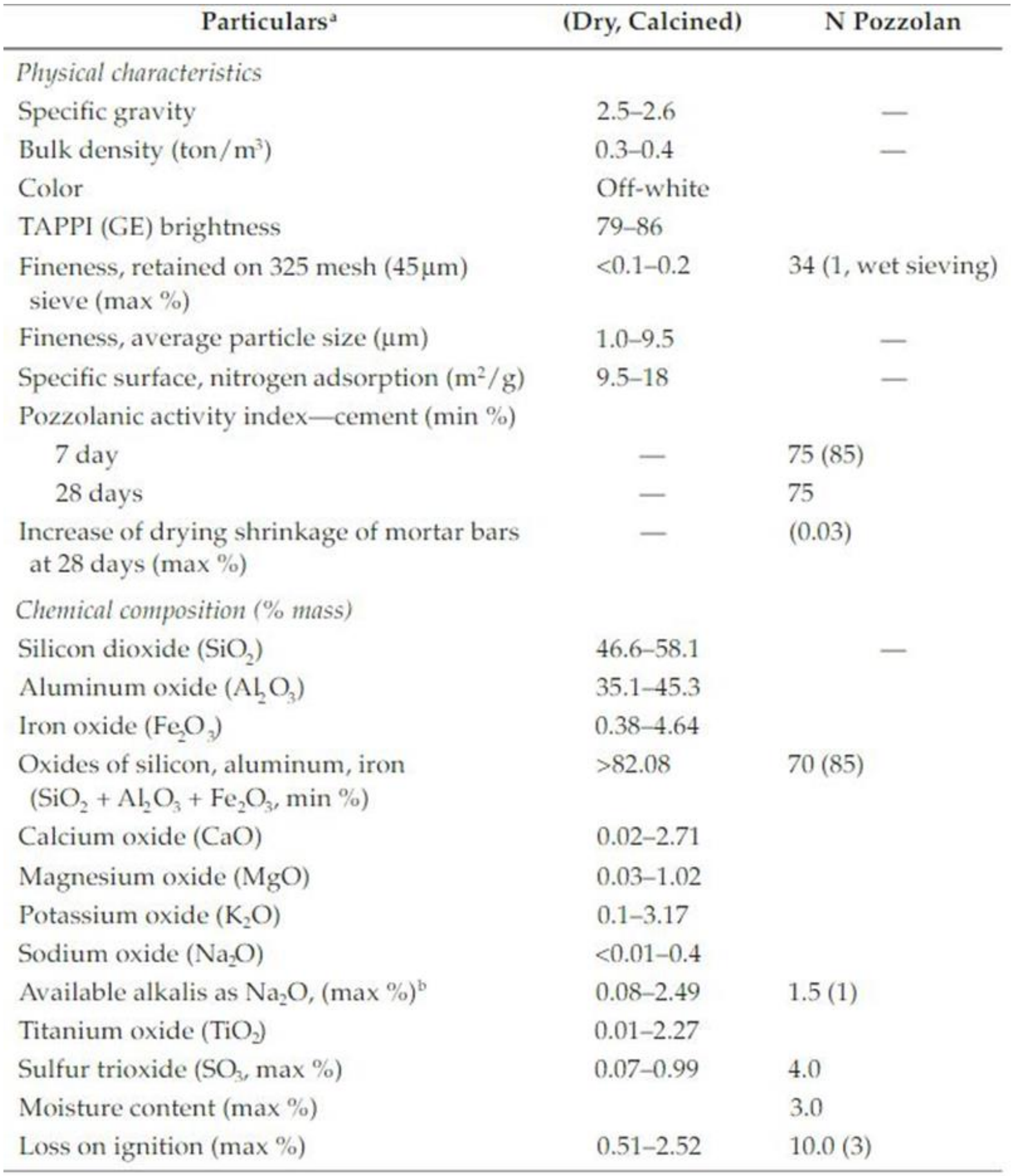
MK is generally white and exhibits a high GE brightness, making it useful in architectural applications. For example, as will be discussed later, MK concrete generally sees high early-strengths which make it ideal for prestressing applications. The most common SCM used for this purpose is SF, and MK has shown itself to be comparable to SF in ability to achieve high early-strength in concrete. The aesthetic difference here being that SF tends to make the concrete darker with its gray color. MK is also typically a very fine material, lying somewhere in-between cement and SF (surface area $\approx 15\ m^2/g$) [19]. 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 Fe_2O_3) tend to implicate a higher purity kaolin base material. 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 [24]. Both alumina and silica contribute to the enhancement of the concrete matrix via the pozzolanic reaction. Generally, MKs with a $Al_2O_3 + SiO_2 + Fe_2O_3$ 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 typical physical and chemical properties of MK can be seen in Figure 1.

The consensus within the literature is that MK contributes to concrete performance in three ways [19, 25]. 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 will be discussed when appropriate in the subsequent sections. The last, and most influential, will be discussed in this section: its role 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 [1]. 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 [26]. 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 [11]. 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 C_2ASH_8 (stratlingite), C_4AH_{13}, and C_3AH_6 (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, as well as accelerating the cement hydration and desifying the paste matrix [25].



Particulars[a]	(Dry, Calcined)	N Pozzolan
Physical characteristics		
Specific gravity	2.5–2.6	—
Bulk density (ton/m^3)	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_2O_3)	35.1–45.3	
Iron oxide (Fe_2O_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_2O)	0.1–3.17	
Sodium oxide (Na_2O)	<0.01–0.4	
Available alkalis as Na_2O, (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 taken from [19]

Metakaolin Usage in the United States

MK is currently used as a SCM in concretes in the U.S., though its usage is not as widespread as that of SF, FA, or blast furnace slag. Specifications for its usage in states other than Georgia and its importance in the markets of Georgia will be discussed.

State Specifications

Although the 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 AASHTO and/or ASTM standards, and it is universal that the MK product being used must be on an approved supplier list of some kind (analogous to qualified products list 'QPL' for the GDOT). However, some states provide additional requirements. The requirements outlined here are current to 2008.

Florida:

- MK conforms to ASTM C618
- has an $Al_2O_3 + SiO_2 + Fe_2O_3$ 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
- be comparable to a SF concrete mixture
- display acceptable strength and durability parameters as per ASTM standards:
- C39 (compressive strength)
- C157 (unrestrained shrinkage)
- C1012 (sulfate resistance)
- C1202 (chloride ion penetrability)

Illinois:

- MK conforms to AASHTO M321

Montana:

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

Nebraska:

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

Nevada:

- Conforms to ASTM C618
- 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

New York:

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

Oregon:

- MK meets AASHTO classification outlined in M295
- 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
- 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%
- If MK is being used to mitigate ASR a 15-25% replacement must be used

Texas:

- Must conform to ASTM C618
- $Al_2O_3 + SiO_2 + Fe_2O_3$ 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 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

Wisconsin:

- MK must conform to ASTM C618

Georgia Market

Georgia is a global leader in kaolin mining and produces over 5.4 million tons per year [12]. 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 [13]. The primary deposits in Georgia lie between Macon and Augusta. However, rich deposits also exist along the portion of the Atlantic Seaboard Fall Line that extends into South Carolina. This fall line that extends through Georgia and into South Carolina is also called the Kaolin Belt. Figures 2 and 3 give context to the location of kaolin mining in Georgia.

Figure 2: Georgia's portion of the kaolin belt [13]

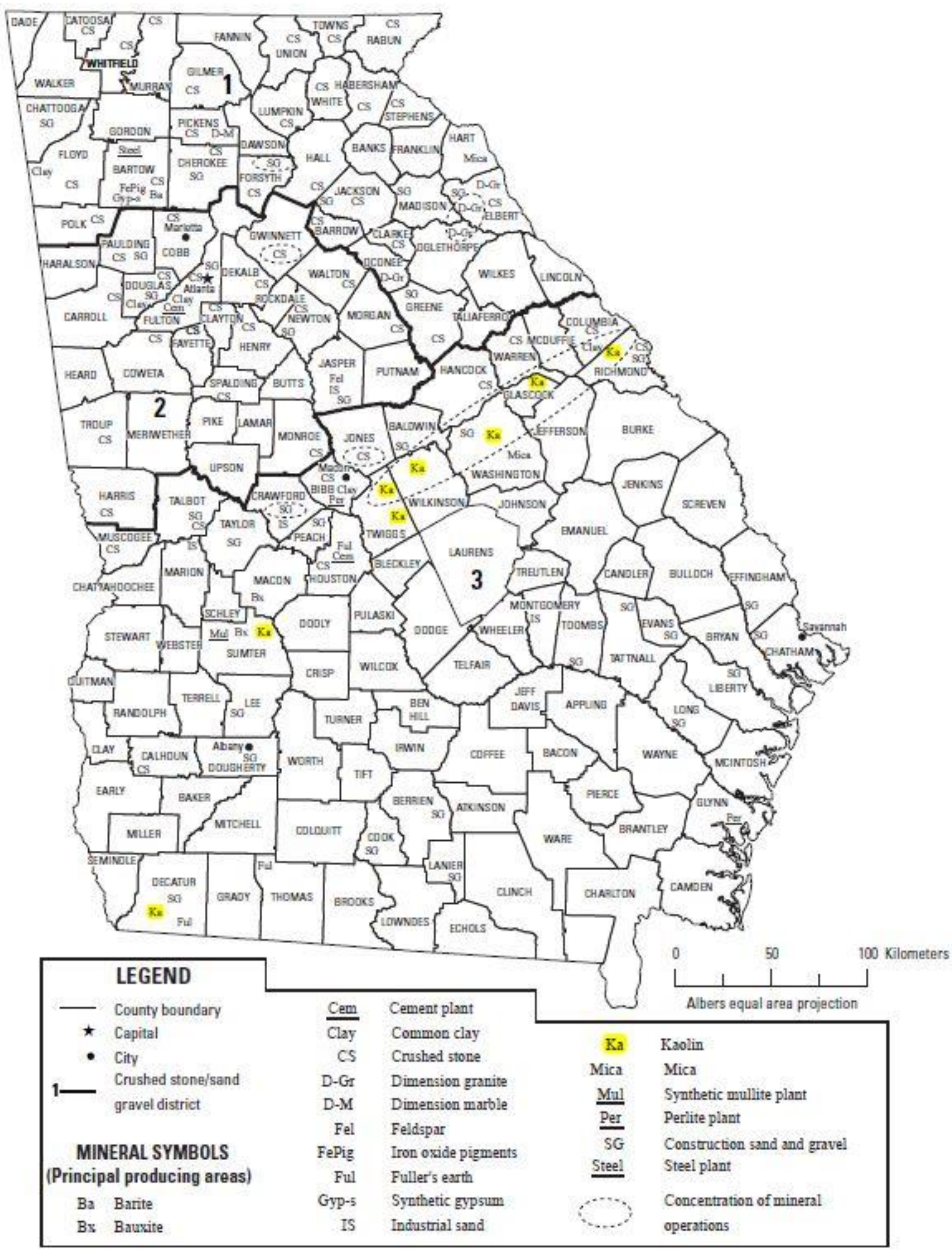


Figure 3: Highlighted locations of kaolin mining in Georgia [12]

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 [27]. 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

Behavior in Binary Cementitious Systems

This section of the paper will cover the effects of the binary inclusion of MK in cementitious systems. Fresh and hardened concrete properties are discussed, including: mechanical properties, durability, dimensional stability, and miscellaneous thermal and chemical characteristics of associated pastes.

Fresh Concrete Properties

In many cases a high range water reducing admixture (HRWRA, also referred to as a superplasticizer) 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 increasing 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. The results of the increase in water demand is that the 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 [28].

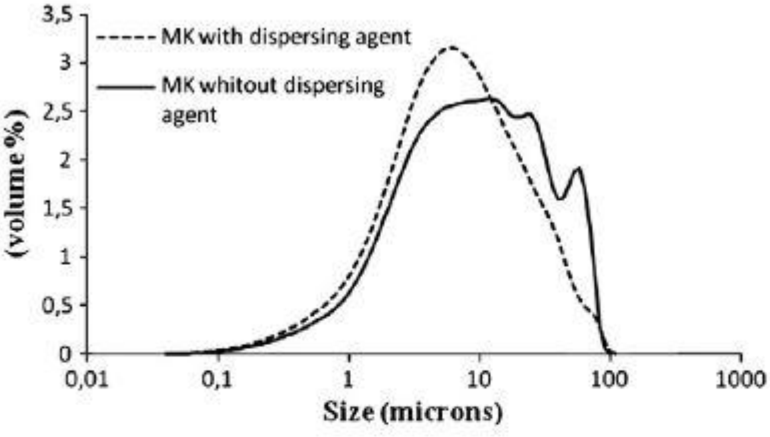


Figure 4: Particle size distribution of metakaolin [28]

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) [28]. 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% respectively by weight.

Paiva et al. studied the effect of a HRWRA on the dispersion properties of concrete mixtures containing 0, 10, 20, and 30% MK [28]. The rheological parameters g and h (yield stress and viscosity, respectively) were studied to quantify the effects of the dispersion on fresh and hardened properties of concrete. It was found that 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. It was also found that these lager agglomerates were less reactive than the individual particles of MK. Small compressive specimens were made, and it was discovered 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 decreased 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 superplasticizer [29]. Li and Ding investigated the effect of MK on workability and found that MK significantly reduces the workability when compared to control mixtures [30].

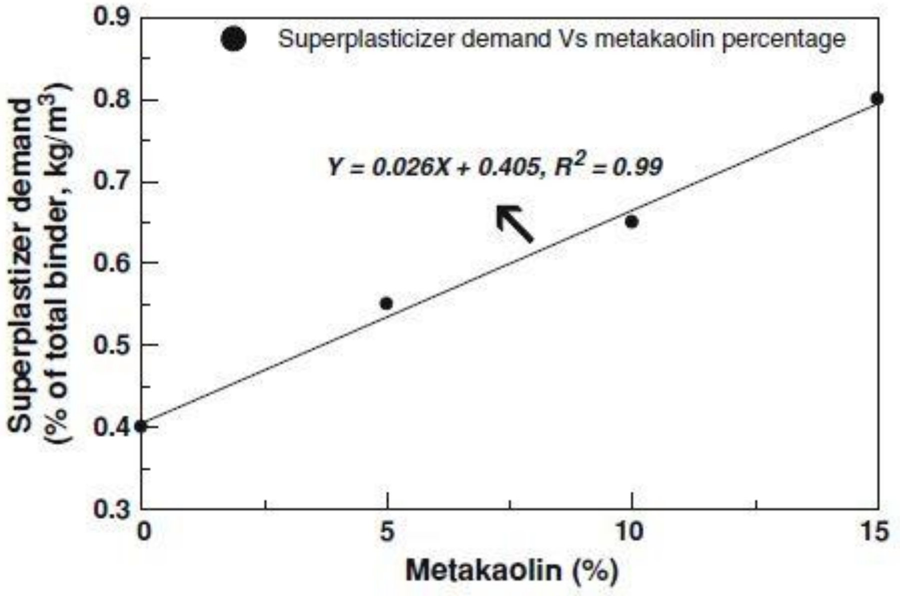


Figure 5: Plasticizer demand as a function of metakaolin replacement level [29]

The review of available literature by Sabir et al. shows that workability reductions can always be expected when mixing MK concretes [26]. This is due in large part to the material fineness of MK. It is interesting to note that in research conducted by Caldarone et al. MK concretes required 25-35% less HRWRA than their SF counterparts [31]. Because SF has a higher surface area and material fineness and a slightly lower pozzolanic activity, this supports an explanation of reduced workability almost exclusively because of material fineness.

There is controversy in the literature as to whether MK increases or decreases setting time. In a study performed by Brooks and Johari it was found that both the initial setting time and final setting time were delayed by the inclusion of MK [32]. With the aforementioned ‘specific dosage’ concept in mind it was shown that the initial setting times in increasing order were 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, with the control being 7.7 hours and the 10% MK being 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. It was observed that both the initial and final set times were lengthened by the addition of MK [33]. 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) being observed between the 10% and 15% MK mixtures [34]. The time to final set varied no more than 36 minutes and did not indicate a systematic trend.

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 (25,400 m^2/kg) reaching initial set 39 minutes before the coarser MK (11,100 m^2/kg). The time from initial set to final set were comparable between both MK blended cements and the control case [35].

Mechanical Properties

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) [36].

Saravanan found that a 20% cement replacement by MK produced the highest compressive strength when combined with a 10% cement replacement by FA. At 28 days their cylinders for the 20% MK replacement averaged at 29.75% increase in strength from the control [37].

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 [28]. 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%. However, when the HRWRA was used to combat the decrease in workability 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 the MK particles which facilitated the production of C-S-H, while also allowing a higher w/cm. Both 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 [24]. The compressive strength gain was also measured SF concrete specimens, and it was found that the rate of strength gains for MK concretes exceeded even the SF concretes. This trend was especially visible at the age of 3 days. The author attributed this to the acceleration of the 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 [38]. The optimum replacement is therefore seen to vary 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 relatively high w/cm ratio (0.50). Another contributing factor is the SiO_2+Al_2O_3 contents of the MK were lower than other studies (here equal to 93.1%). It was found that the rate of strength gain was significantly higher in MK concretes up to 14 days of curing and was then seen to diminish. However, strengths at all ages were higher than the control.

Dinakar et al. observed a maximum compressive strength at a 10% MK replacement with SiO_2+Al_2O_3 contents equal to 92.6%, and a w/cm ratio of 0.30 [29]. 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 [33]. This is most likely due to the low pozzolanic activity of their MK (SiO_2+Al_2O_3 = 46.73%). It is interesting to note that the 5% MK mortar was the only replacement to meet their 52.5 MPa (7,600 psi) minimum at 90 days of curing.

A review of literature by Sabir et al. saw that generally there is little benefit beyond a 15% MK replacement level for compressive strength [26]. 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 [39]. Strengths were found to systematically increase with the addition of MK up to 15%. Interestingly, all concretes at a w/cm of 0.50 displayed higher compressive strengths than those of 0.60. Even the w/cm = 0.50 control performed better than the w/cm = 0.60 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 [40]. The MK that was used had a combined Al_2O_3+SiO_2 content equal to 95.89%, for which a significant portion (63.53%) was SiO_2. The Blaine's specific surface area was 1,177 m^2/kg. The results indicate that mortars containing MK achieve compressive strengths greater than control at all ages other than 1 day. However, it is interesting to note that the 5% MK mortar's 1-day compressive strength was greater than the control. The magnitude of compressive strength increases 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 is contributed to the internal stresses induced in the MK specimens. The author 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) [41]. The Al_2O_3+SiO_2 content of the MK was equal to 96.40%. The 9% MK concrete performed the best with a 30% increase in compressive strength over 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%. It was observed that 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 [42]. 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 used MK to replace cement.

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 [43]. 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. However, at a w/cm ratio equal to 0.35 the MK blended concrete significantly out-performed the SF blended concrete. It is noteworthy that 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 varying w/cm ratios equal to 0.5, 0.4, and 0.35, and at 7, 28, 90, and 180 days of curing [8]. The MK used was highly siliceous (SiO_2 = 74.3%, Al_2O_3 = 17.8%), and had a Blaine's specific surface are equal to 0.37 m^2/kg. Typical patters 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 [35]. A trend of increasing strength with decreasing w/cm was observed, as is generally expected. The finer MK (25,400 m^2/kg) achieved higher ultimate strengths, as well as displaying a much higher rate of strength gain. The strengths observed in the finer MK at 3 days is comparable to the strengths observed from using the coarser MK (11,100 m^2/kg) at 7 days of age. The most notable increases in compressive strength from control are the finer MK at 1 (38.1% greater than control) and 90 (39.2% greater than 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 [44]. The strengths at all ages are seen to be greatest for MK, followed by SF, GGBS, and the control, respectively. Shekarchi et al. saw that concrete with 15% MK replacement of cement saw compressive strength increases of 20% over control [34].

The modulus of rupture (MOR) and the split-cylinder tests (ASTM C78 and C496, respectively) are the two most common tests in determining the 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. Ultimate tensile stresses calculated from MOR tests tend to produce higher values than their split-cylinder counterparts. In test conducted by Olanike it was shown that split-cylinder strengths of concrete tend to be 60%-80% of the MOR [45].

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 [29]. The replacement of 10% resulted in a 5.15% increase in the splitting tensile strength. This optimum replacement percentage is consistent with findings for compressive strength.

Jiang et al. observed that at all curing ages the flexural capacity of MK mortars was lower than control at a w/cm ratio of 0.17. However, it was found that MK mortars containing steel fibers were stronger than the control fiber mixture in flexure [11]. It should also be noted that the highest flexural strength was seen at a 10% MK replacement level with the inclusion of steel reinforcing fibers. The author contributes this to the MK enhancing the bond between the steel fibers and the rest of the paste. The inclusion of both MK and the 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 indicate that a low-reactivity MK will decrease flexural strength systematically with replacement level [33]. 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 [40]. The MK that was used had a combined Al_2O_3+SiO_2 content equal to 95.89%, for which a significant portion (63.53%) was SiO_2. The Blaine's specific surface area was 1,177 m^2/kg. It was shown that the flexural strength of the mortars containing MK was greater than the control at all ages other than 1 day. Increases in flexural strength were between 3% and 14% higher than 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 [43]. 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 out-performed both the control and SF concretes at all ages. It is especially noteworthy that the 15% MK at 7 days of curing out-performed the 15% SF at 28 days of curing.

Justice and Kurtis report that increases in flexural strength observed using MK were in the range of 1-2 MPa (145 psi – 290 psi) [35]. It was also reported that 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 by using the finer MK was equal to the 3-day strength attained by using 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.

The effect of the addition of 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 Microns Limited, Gujarat) replaced OPC with 0%, 7.5%, 10%, 12.5%, 15%, and 17.5% and found that the best results were achieved with a 10% replacement, showing a 26.44% increase in the MOE [36].

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, equaling to 47.16 MPa (6,840 ksi, a 3.8% increase from control) [29].

Justice and Kurtis observed an increase in the MOE when using MK as an 8% replacement of 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 [35]. 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.

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 that a poor correlation between resistance to alkali silica reactions and the rest of the durability parameters existed [34]. 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%.

Poon et al. studied the permeability of MK and SF concretes by chloride ions using ASTM C1202. 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. 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 did 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 [24]. 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, and therefore greatly influencing the transport properties. Interestingly, Poon et al. studied the correlation between the concrete and paste-matrix porosity and the chloride ion permeability. It was found that 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 [29]. The control specimen passed a total of 1,162 Coulombs in the span of 6 hours, which is classified as a low chloride penetrability by ASTM C 1202. In contrast, all specimens including MK indicated a very low permeability, with the lowest total charge passed being 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 being 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 [46]. However, the coefficients remained within the same range of one another (10^{-4} m^2/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 as they pertain to chloride ion transport are especially significant because of chloride ions relationship to the corrosion of reinforcing steel [46].

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) [41]. The Al_2O_3+SiO_2 content of the MK was equal to 96.40%. The concentrations of the unbound chloride ions in the pore solution was 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. It was found at a given depth, 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 control by replacing 9% of the cement by MK. The chloride binding capacity was also studied with the additional replacement of 5% cement with gypsum ($CaSO_4 \cdot 2H_2O$). The results indicate 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 C_3A 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 [42]. Chloride ingress experiments indicate that chloride content at all depths of specimens containing MK, 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 a MK that contained normal amounts. It was discovered that the total chloride ion concentrations (free + bound), as well as the free chloride ion concentrations, decreased with successive MK replacements. It is concluded that the alumina content of the MK increases the chloride binding capacity of the concrete, and that as the binding capacity increases the chloride diffusion coefficient (measure of chloride diffusion into concrete) decreases.

Corrosion of the steel reinforcement inside of concrete structures plays a large role in the service life of the structure. Furthermore, the movement of chloride ions inside of concrete contribute significantly to the corrosion of steel by removing the passive oxide coating [42]. The corrosion of the steel results in voluminous reaction products, which then leads 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.

C_3A 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 Al_2O_3 content than the SiO_2 content [47]. The chloride binding capacity of the concrete will determine to which extent the intrinsic chloride ions will be made stable. 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 decreasing w/cm ratio. In addition, there was a systematic decrease in total charge passed with increasing replacement levels of cement by MK [8]. The 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 penetrability 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. 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 R^2 value equal to 0.96.

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 of concrete [48]. The experimental setup entailed concrete cylinders which contained steel rebar and were partially submerged in a chloride solution. The steel bars were connected to a power supply that sustained a constant potential of 30 Volts, and the indication of failure was the cracking of the concrete specimen. It was observed that concrete incorporating MK was effective at delaying the age at failure. The best protection was offered at 15% MK, the specimens for which 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%.

Ramlochan et al. observed that in cases where MK was used the expansion of the specimens decreased as the level of replacement increased [49]. 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 the concrete prism tests required only a 10% replacement by MK. This is consistent with field studies that show the high rate of false positives while using the accelerated mortar bar method [50].

A substantial benefit from the use of pozzolans as a partial replacement of 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 by the use of two separate reactive aggregates: a siliceous limestone and a greywacke-argillite gravel. In addition, pastes 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 [49]. 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

2-year period to monitor various ion concentrations ($(OH)^-$, Na^+, and K^+). The results showed that at 7 days, all replacements displayed much lower pore solution alkalinity than the control pastes. Beyond 7 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% replacement reduced the hydroxyl concentrations to less than 0.20-0.25 mol/L, which is believed to be the threshold to maintain ASR [51]. The results of the concrete prism test show that the limestone aggregate at all replacement levels exhibited higher expansions than did the greywacke-argillite gravel. At the age of 2 years, only the 20% MK replacement passed the limit criteria, while for the greywacke-argillite gravel both 10% and 15% MK passed. Using the accelerated mortar bar method, it was shown that 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 [50].

Kostuch et al. was able to completely reduce the expansion due to ASR by replacing 15% of OPC with MK [52]. The expansive product was found to be a gel with high concentrations of Ca^+ ions and was linked to the available CH/SiO_2 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 of cement at 5%, 10%, 15%, and 20% abiding by the test methods as per ASTM C 1260 [40]. As with their results with sulfate attack, the 5% MK mortars exhibited lower expansions than the control, but not as significantly as those containing 10%-20% MK. The author notes that 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 SiO_2 to form additional C-S-H gel, and thus reduces the available alkalis.

A study was conducted by Khatib and Wild on the influence of MK on the sulfate resistance of mortar bars. It was determined that a replacement level of 15% MK was necessary to provide good sulfate resistance [38].

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 C1020 [40]. According to ASTM C 1012, the 6-month expansion limit is 0.10% of the original specimen length. 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 Na_2SO_4. In the same study an experiment was also conducted at a sulfate concentration of 150 g/L Na_2SO_4 and, while the expansion values were higher than the previous test, it was shown that 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: the MK replacement of cement results in a decrease in C_3A, and the permeability decrease reduces ingress of sulfate ions into the pore solution.

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 [39]. The author 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 author speculates 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 [40]. It was found that the mortars containing absorbed less water than the control mortar (7.8% of weight of specimen). Furthermore, as with compressive and flexural strengths, the optimum percentage was seen 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. Furthermore, it is also apparent that at higher cement replacement levels (here 20%) there is a substantial benefit, with the largest reduction at 20% MK (sorptivity 41.2% lower than control). All mixtures had a w/cm ratio of 0.50 [42].

Guneyisi et al. found that at a w/cm ratio equal to 0.25 a cement replacement of 15% by SF achieved the greatest decrease in sorptivity from control [43]. However, at a w/cm ratio equal to 0.35 a 15% replacement of cement by MK was found to be optimal. In contrast to the gas permeability, the SF blended concretes displayed a much greater change in response to the changing w/cm ratio, while the MK blended concretes displayed consistency among them. 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. Firstly, its test methods closely resemble the manner in which concrete transports water (and therefore deleterious substances) in the field. Secondly, 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 [8]. 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.

Guneyisi et al. observed the effects on concrete by changing w/cm ratios and employing 5% and 15% replacements of cement by MK and SF [43]. 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. While 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 nearly equivalent in their benefit in reducing the gas permeability of concrete.

Carbonation is the dissolution of CO_2 into the pore solution of a concrete specimen which reacts with the CH to produce calcium carbonate ($CaCO_3$). Barbhuiya et al. conducted carbonation indication tests by placing concrete specimens in a 5% CO_2 cabinet for a period of three weeks [39]. 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 author found that at both w/cm ratios (0.50 and 0.60) the carbonation depth increased with higher replacements of MK except for the 10% MK addition at a w/cm of 0.60. 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. The author indicates that the reduction in porosity may not have been able to counteract the detrimental loss of the CH in the pore solution.

Dimensional Stability

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 [53]. Typically, the effects of the autogenous shrinkage are small in comparison with drying shrinkage. However, in very lower w/cm ratios (less than ~ 0.45) autogenous shrinkage can make up a significant portion of the overall shrinkage [1].

Brooks and Johari studied the effects of varying replacement levels of MK (0, 5, 10, and 15%) on both the 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 [54]. It was found that with increasing replacement levels of MK the early-age autogenous shrinkage decreased with the greatest reduction at 15% MK being 65%. This was attributed to the dilution effect, or the reduction of the amount of cement. In addition, the 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 the 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 control and 15% MK seeing a 56% increase from control. Cumulative autogenous shrinkage (the sum of early-age and long-term) was therefore seen to be higher than control at a 5% MK replacement, and lower for the 10%

and 15% MK mixtures. It is worthy of mention that 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 the drying shrinkage of concrete specimens. Drying shrinkage was calculated as the total shrinkage withholding the autogenous shrinkage. It was found that with the inclusion of MK the drying shrinkage was reduced at all replacement levels, and that the replacement level had little effect on the magnitude of reduction [54].

At low w/cm ratios the total shrinkage is reduced as the replacement of MK increases. As previously mentioned, it has been found that at low w/cm ratios and the lower porosity and finer pore structure that results from the use of MK promote water loss by self-desiccation as opposed to water loss to the environment. Furthermore, it has also been proposed that at higher replacement levels by MK, tetracalcium aluminate hydrate (C_4AH_{13}) is replaced by the more voluminous gehlenite hydrate (C_2ASH_8), which in turn reduces the significant autogenous shrinkage that is observed with MK and SF concretes [54].

Brooks and Johari were some of the first to study the creep response of MK concretes at varying replacement levels in 2001 [54]. In their study compressive creep was observed at a stress to ultimate strength ratio equal to 0.20, while load-free specimens were made 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 strain of the load-free specimens. It was found that at increasing MK replacement levels both the total and basic creep decreased. This is not surprising, and is attributed to the 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. 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 C_2ASH_8 and decreased amount of C_4AH_{13} [55].

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 [53]. The MK used contained high amounts of Al_2O_3 and SiO_2 (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 early-age, and the inclusion of MK decreased long-term autogenous shrinkage. At length scales 0-30 days, the 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 were 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 (C_4AH_{13}) by the less dense gehlenite hydrate (C_2ASH_8).

Guneyisi et al. conducted unrestrained drying shrinkage tests as per ASTM C157. The length measurements were taken every 24 hours for the first three weeks, and then three times per week up to 42 days [43]. The tests indicate 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. It was found that in descending order, the level of performance of the specimens were: 15% SF, 15% MK, 5% SF, 5% MK, and control [43].

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 [53]. For both water contents, it was 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. It was shown that autogenous shrinkage is much higher in the 0.30 w/cm pastes. The results also indicate that the ability of MK to reduce autogenous shrinkage is more efficient at higher w/cm ratios. The use of 20% MK in the w/cm = 0.50 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.

Effects on Chemistry and Structure of Cement Pastes

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 [56]. This was especially prominent in the 10% and 15% replacements. This can be attributed to the reduction in water by the MK. MK's high specific surface area promotes mass adsorption of the water, which delays the hydration of the cement. Similar trends can be seen at 1-8 hours of hydration, where the cumulative heat of hydration (J/g) for all MK replacement levels is lower than that of control. However, at 120 hours 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 did 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 [11]. 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. The results seem to support the explanation that up to a point the combined effects of the acceleration of the 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 of the heat of hydration.

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 was found to contain 11.9% CH by mass of cement, while the 30% MK concrete was found to contain 1.6% [28].

The reactivity of thermally treated and mechanically treated kaolins were 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 indicates that mechanical activation of kaolin is competitive with respect to reactivity to that of thermal activation [21]. Furthermore, the study shows that the percentage of kaolinite determines the level of reactivity between different kaolins.

Subasi and Emiroglu performed pozzolanic reactivity tests on a low-reactivity MK according to ASTM C311 [33]. The results indicate that the pozzolanic activity of mortars at a 20% MK replacement change over time, with the pozzolanic activity of 77% at 7 days of curing and 82% at 28 days.

Subasi and Emiroglu performed x-ray diffraction (XRD) on pastes with 0-30% MK, and there is a decrease in CH in all pastes containing MK. The reduction is minimal at 5% and more significant at all other replacement levels. In addition, after 10-30% replacements seem to have comparable CH peaks as compared to one another, indicating that the low-pozzolanic activity corresponds to a lack of ability to consume much additional CH past a 10% MK addition [33]. 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. states that fully-hydrated ordinary portland cement (OPC) produces 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 [26]. Some of these products are additional C-S-H gel, calcium aluminate hydrates, and alumino-silicate hydrates (some are C_2ASH_8, CS_4AH_{13}, and C_3AH_6). Sabir states that the formation of crystalline products primarily depends on the $Al_2O_3 \cdot 2SO_2/Ca(OH)_2 \cdot (AS_2/CH)$ contents. Furthermore, they type and amounts of hydration products depend heavily on OPC composition, MK purity, and w/cm ratio. A review of the literature available in 2001, performed by Sabir et al., indicates that a 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 was observed at 14 days of curing, which indicates that at this age the rate of CH consumption by MK is much greater than the rate of CH production by the OPC [25].

Coleman and Page showed that up to a replacement level of 20% MK, the Cl^- to $(OH)^-$ ratio in the pore solution is comparable to that of OPC mixtures [57]. The conclusion being drawn is that although a decrease in pore solution pH was observed, a replacement level of 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 [25]. MK, which also contains a high percentage of Al_2O_3, also forms hydration products such as C-A-H and C-A-S-H which are believed to assist in the cementitious process and contribute to strength.

Barbhuiya et al. note 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 [39]. The study also indicated that the relative proportions of C-S-H gel are affected by the inclusion of MK. Nanoindentation results indicate that the addition of MK promotes 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 of paste specimens. An increased amount of CH relative to control at early ages of hydration (~8 hours) indicate that cement hydration is accelerated by including MK [35]. A decrease in CH content from 7 to 28 days of hydration also indicates that the pozzolanic reaction is continuing to consume more CH than is being produced after 7 days. Interestingly, the material fineness affects the consumption rate of CH. The results indicate that the finer MK consumes CH at faster rates at early ages, but the coarser MK consumes more CH by the 28-day mark. A reduction in CH is generally 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. SEM photographs illustrate that the inclusion of SCMs increase the uniformity of the paste surrounding the aggregates, as well as decrease the size and frequency of microcracks. In addition, the micrographs indicate that the addition of SCMs result 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. It was found that in the OPC system monosulfoaluminate is more stable than the phase assemblage of ettringite and C_3AH_6 at temperatures > 5°C [44]. However, when silica is introduced via a SCM the phase assemblage of ettringite and C3AS0.8H4.4, which is a member of the solid solution $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$, results in a lower Gibbs free energy of reaction. This indicates that these phase assemblages are more thermodynamically stable when SCMs are used in concrete mixtures [44].

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 was found to reduce the average pore diameter and the MIP porosity [24]. This 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 [11]. As compared to FA and SF, MK has a coarse and irregular particle surface which has a higher yield stress and viscosity, and therefore entrains more air. This makes intuitive sense, as these rheological parameters should increase with a decrease in workability, and this explanation is consistent with the findings of Paiva et al. [28].

A review of literature by Sabir et al. indicates that the average pore size decrease with the addition of MK [26]. Specifically, in a study conducted by Bredy et al. it was seen that at a replacement level of 30%, the pores were typically narrow-necked pores with a diameter of less than 0.03 μm [58].

Barbhuiya et al. found a reduction in porosity resulted from a 10% MK specimen, at a w/cm of 0.40, over control [39]. 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 [42]. 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. This was found in the mixture with a 10% replacement of cement by a poor Greek kaolin.

SEM images taken by Ramezanianpour and Jovein indicate that by 28 days of curing, pastes containing MK are more compact and uniform. This was not as evident at 7 days of curing. A reduction in the frequency of ettringite crystals was also observed and were replaced by additional calcium silicate hydrates and calcium aluminosilicate hydrates [8]. In addition, XRD was performed on paste samples and supports 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 [35]. Furthermore, a finer pore structure was observed with the finer MK than the coarser MK. This corresponds to 63%, 57%, and 43% for the finer MK, coarser MK, and 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 SCMs. MIP results indicate that the overall porosity decreases with the addition of all SCMs, and that the average pore diameter decreases with respect to the control. In decreasing order of effectiveness of the SCMs were MK, SF, and GGBS [44]. Fine SCM particles can be seen to fill gaps between cement particles, densifying the paste matrix. Furthermore, 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 show that the inclusion of SCMs increase the strength of this region. Microhardness can also be seen to increase with curing time, as is expected with OPC concretes. A summary of the effects of MK inclusion in binary cementitious systems is presented as Table 1.

Table 1: Summary of metakaolin concrete properties

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	Increase / Decrease	Meland et al., 1983); Alshamsi (1997);
CTE	Unknown	N/A

Behavior in Ternary Cementitious Systems

Combinations of MK with FA and slag have been reported in the literature and are discussed in this section.

At a w/cm of 0.41 Saravanan studied concrete mixtures with a constant 10% 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 – highest strength being 58.66 N/mm^2 at a 20% replacement by MK [37]. 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 sorptivity was also measured, which is the one-dimensional measure of capillary movement in a porous substance and was found to systematically decreased as the percentage of MK increased.

Sabir et al. notes that in several studies where SCMs that 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 [26]. 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.

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 [38]. 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 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 control as early as 1 day of curing for up to 30% GGBS. Khatib and Hibbert noticed here that the MK replacement level that provided optimum compressive strength changed as the level of GGBS changed. With no MK, the optimum replacement by GGBS was 50% [38]. 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 the results of a high MK contents is that 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 with 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 [59].

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 [60]. The GGBS used in this study was a “ultra-fine” slag with a Blaine’s specific surface area of 630 m^2/kg. As a comparison the MK used in this study had a Blaine’s specific surface area of 310 m^2/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 as compared to control. The compressive strengths of specimens were also taken at 3, 7, and 28 days of curing and it was found that 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 exceed the binary MK and OPC mixtures. XRD indicates that the binary MK (reference), and 10% MK with 30% GGBS mixtures contain a higher concentration of AFt phases at 28 days of curing. XRD results also show 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 produce a heat of hydration less than OPC mixtures [61].

CHAPTER 3

EXPERIMENTAL METHODS

This section discusses the design methodology, experimental design, and experimental protocol associated with answering the research questions presented in Chapter 1.

Design of Experiment

As previously mentioned, the goal of this study was to explore the efficacy of MK as an alternative SCM to FA, and secondarily to provide recommendations for its usage in concrete. FA is a versatile SCM in that it is able to improve the fresh properties of concrete, increase durability, as well as reduce liberated heat in mass concreting [5]. Binary and ternary SCM combinations using MKs are evaluated for this purpose. It is for this reason that it is so widely used. The experimental study conducted in this paper will use a typical GDOT drilled shaft concrete design as a benchmark. As will be discussed, this represents a 45% replacement of cement by FA. Therefore, ternary SCM combinations shall replace a portion of cement equaling 45%. Concrete mixtures will be proportioned such that they meet applicable GDOT standards for fresh and hardened concrete properties.

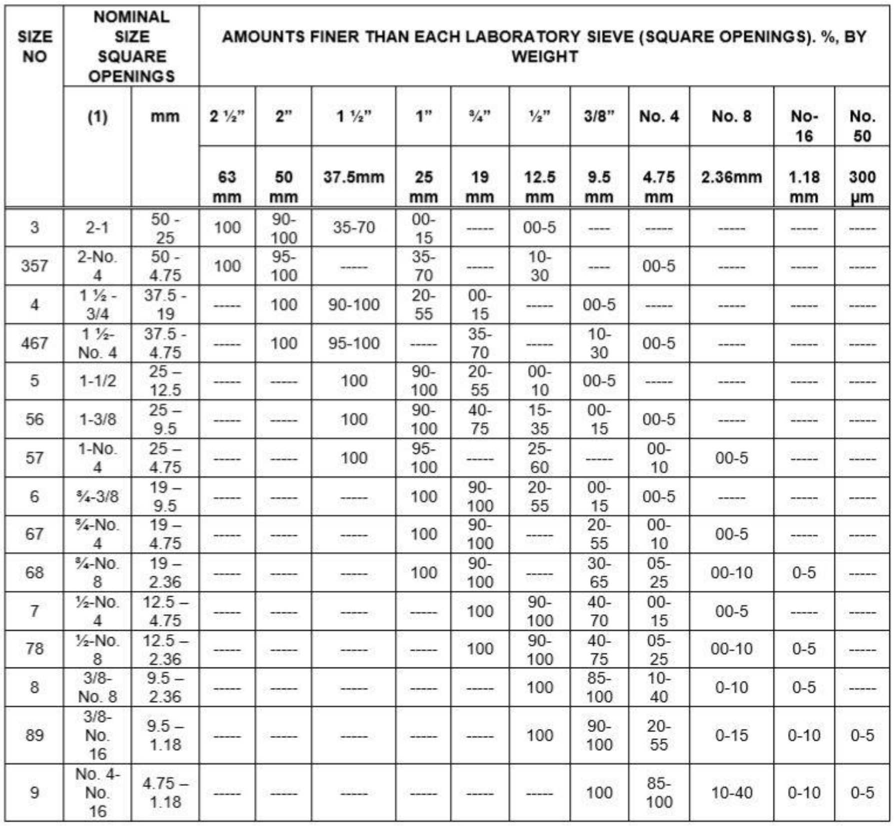
Nineteen unique combinations of SCMs were evaluated; one of which being an OPC control mixture. Three commercial MK products were evaluated as binary replacements of cement. Each product will replace cement by 10%, 15%, and 20% by weight. These are the most typical replacement levels in the literature, and these mixtures will help inform specifications for binary MK concretes. In addition, six ternary mixtures will be performed with MK and slag; all possible combinations of three MKs and two slags. The replacement of cement will amount to 15% by each MK and 30% by each slag, equaling the total cement replacement level of 45%. The choice of a 15:30 MK:slag replacement ratio was chosen because a study conducted in the same laboratory as this study concluded that a 15% MK and 30% slag combination resulted in the lowest heat of hydration at a 45% replacement level [62]. Two slag products will be used to contextualize the variation in performance of the MKs. Finally, three binary mixtures will be performed which include the two slags at a 30% replacement of cement, and a high-volume FA mixture (45% replacement). These will serve as additional benchmarks to evaluate the performance of the ternary SCM blends.

Applicable GDOT Specifications

Coarse aggregate must be made of crushed stone, gravel, or synthetic aggregate and must be inert. Soundness tests require a mass loss of less than 15%. In addition, the GDOT has specified that the following limitations be observed: micha schist (as defined by ASTM C 294) 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%. Coarse aggregates must have a gradation that meets a standard size (Table 2). For portland cement concrete pavements, only coarse aggregate size Nos. 467, 67, or 57 are permitted. Specified sizes for coarse aggregates used in structural concrete vary by concrete class (Table 4).

Fine aggregates may consist of natural sands, manufactures sands, or a blend. A fine aggregate made from reactive coarse aggregates will demonstrate the same deleterious behavior, and their usage is forbidden. 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) analysis conducted on the material retained on the No. 16 sieve must be used to determine these percentages. As with coarse aggregates, fine aggregates must conform to a standard size (Table 3). For portland cement concrete pavements, only fine aggregate size No. 10 is permitted.

Table 2: GDOT standard sizes for coarse aggregates

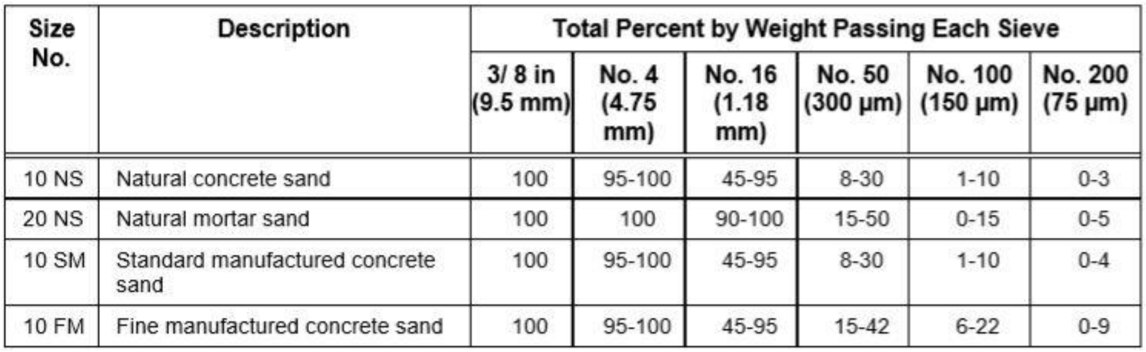


SIZE NO	NOMINAL SIZE SQUARE OPENINGS		AMOUNTS FINER THAN EACH LABORATORY SIEVE (SQUARE OPENINGS). %, BY WEIGHT										
	(1)	mm	2 ½"	2"	1 ½"	1"	¾"	½"	3/8"	No. 4	No. 8	No-16	No. 50
			63 mm	50 mm	37.5mm	25 mm	19 mm	12.5 mm	9.5 mm	4.75 mm	2.36mm	1.18 mm	300 µm
3	2-1	50 - 25	100	90-100	35-70	00-15	-----	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	-----	-----	100	90-100	40-75	15-35	00-15	00-5	-----	-----	-----
57	1-No. 4	25 – 4.75	-----	-----	100	95-100	-----	25-60	-----	00-10	00-5	-----	-----
6	¾-3/8	19 – 9.5	-----	-----	-----	100	90-100	20-55	00-15	00-5	-----	-----	-----
67	¾-No. 4	19 – 4.75	-----	-----	-----	100	90-100	-----	20-55	00-10	00-5	-----	-----
68	¾-No. 8	19 – 2.36	-----	-----	-----	100	90-100	-----	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	-----	-----	-----	-----	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

Cements (Type I-V) must conform to the low alkali and false set requirements of AASHTO M85. Water must be potable. Additionally, the alkalinity as calculated in terms of calcium carbonate, total organic solids, total inorganic solids, and sulfate (SO_4)

contents may be no greater than 0.05%. The chloride content may be no greater than 0.01%. For a GDOT Class I pavement, a minimum cement content of 541 pcy (320 kg/m^3) 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 pcy (335 kg/m^3) is required in addition to a maximum w/cm of 0.50. For both mixtures the design air content range is 4.0%-5.5%, with the minimum allowed being 3.0% and the maximum being 6.5%. Minimum cement contents, maximum w/cm ratio, acceptable slump values, and acceptable air contents vary by class for structural concrete (Table 4).

Table 3: GDOT standard sizes for fine aggregates

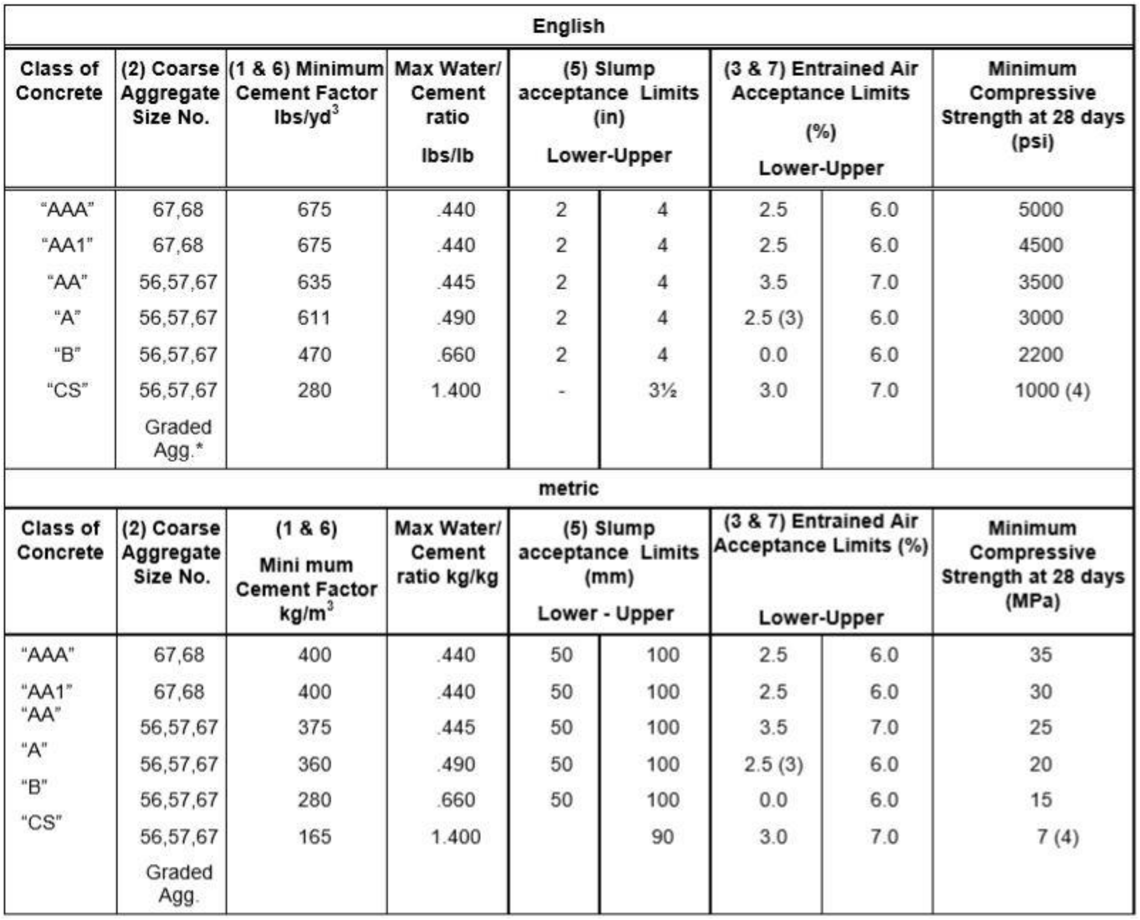


Size No.	Description	Total Percent by Weight Passing Each Sieve					
		3/ 8 in (9.5 mm)	No. 4 (4.75 mm)	No. 16 (1.18 mm)	No. 50 (300 µm)	No. 100 (150 µm)	No. 200 (75 µm)
10 NS	Natural concrete sand	100	95-100	45-95	8-30	1-10	0-3
20 NS	Natural mortar sand	100	100	90-100	15-50	0-15	0-5
10 SM	Standard manufactured 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

Chemical admixtures must be present the GDOT’s QPL-13 or QPL-14 to be used in concrete mixtures. Similarly, mineral admixtures (SCMs) must be present on QPL-30 to be used. Chemical admixtures must also meet the physical, uniformity, and equivalence requirements in AASHTO M194 for types A, B, C, D, E, F, or G. They are not permitted to contain more than 0.80% chlorides, as calculated by calcium chlorides. The only SCMs currently contained within GDOT QPL-30 are FA and blast furnace slag. However, SCMs that are outlined in GDOT Standard Specifications include: FA, raw or calcined natural pozzolans, GGBS, and SF. FA (Classes C and F) and Class N pozzolans shall meet the requirements in AASHTO M295. Any GGBS used shall conform to

AASHTO M302, and SF to AASHTO M307. The current presence of MK in GDOT's specifications is therefore superficial until it appears on a QPL and contains additional restrictions on quality and usage. SCMs are currently permissible in GDOT concrete pavements. The use of FA and BFS is allowed given that the mixture design does not exceed the allowable percentage replacement for each. For FA the maximum percentage of replacement allowed by mass is 15%. This is also the case for structural concrete. Blast furnace slag can 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), and high early-strengths are not needed. If projected temperatures are less, the percentage replacement by GGBS is restricted to 30%.

Table 4: Various requirements for GDOT structural concrete by class



English

Class of Concrete	(2) Coarse Aggregate Size No.	(1 & 6) Minimum Cement Factor lbs/yd³	Max Water/ Cement ratio lbs/lb	(5) Slump acceptance Limits (in) Lower-Upper		(3 & 7) Entrained Air Acceptance Limits (%) Lower-Upper		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 Graded Agg.*	280	1.400	-	3½	3.0	7.0	1000 (4)

metric

Class of Concrete	(2) Coarse Aggregate Size No.	(1 & 6) Mini mum Cement Factor kg/m³	Max Water/ Cement ratio kg/kg	(5) Slump acceptance Limits (mm) Lower - Upper		(3 & 7) Entrained Air Acceptance Limits (%) Lower-Upper		Minimum Compressive Strength at 28 days (MPa)
"AAA"	67,68	400	.440	50	100	2.5	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 Graded Agg.	165	1.400		90	3.0	7.0	7 (4)

Materials

Three MK products are evaluated. The first product (MK1) is sourced from Sandersville, Georgia. The second product (MK2) is sourced from Aiken, South Carolina. The third MK (MK3) is sourced from Sandersville, Georgia. All MK products used in this study are high-reactivity MKs (HRMs) that conform to ASTM C 618. The consensus within the literature is that a HRM is any MK which contains $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 90\%$ by weight. As all MKs evaluated in this paper are HRMs, they will simply be referred to as MKs. Although the reactivity of any MK is entirely dependent on the percentage of kaolinite that is dehydroxylated during calcination (amorphous, or 'glassy', alumina and silica), 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 typically good predictors of quality. A combination of physical and chemical characteristics of the MKs used in this study are found in Table 5. Pictures of each product are shown in Figure 6.

Two, Grade 120, commercially available slags were used in this study. As with MK, the chemical composition and physical characteristics are important in understanding slag behavior once inside the concrete. Select physical and chemical properties for the slags are presented in Table 5. The FA is an ASTM C618 Class F FA. Pertinent physical and chemical properties for the FA is also included in Table 5. Finally, a Type I/II portland cement conforming to ASTM C150 was used for all concrete and mortar mixtures. The cement is local to Atlanta, Georgia. Table 5 lists the physical and chemical characteristics, as well as the calculated Bogue phase composition. The material data for all cementitious materials were provided by the material manufacturing companies. All cementitious materials other than the MKs used are GDOT qualified products and appear on QPL-30.

Table 5: Physical and chemical properties of cementitious materials used in this study

		Cement	MK1	MK2	MK3	SLa	SLb	FA
Chemical	SiO_2	19.70%	50.75%	54%-56%	51.66%	33.33%	34.07%	50.77%
	Al_2O_3	4.70%	45.91%	40%-42%	43.99%	13.50%	12.73%	26.65%
	Fe_2O_3	3.00%	0.45%	< 1.4%	0.47%	0.68%	0.47%	3.76%
	CaO	63.30%	0.06%	< 0.1%	0.01%	41.28%	40.41%	11.30%
	MgO	3.10%	0.00%	< 0.1%	0.03%	5.53%	6.56%	2.15%
	Na_2O	*	0.23%	< 0.05%	1.89%	0.21%	0.17%	1.17%
	TiO_2	*	1.87%	< 3%	1.89%	1.89%	0.52%	*
	SO_3	3.20%	0.08%	< 0.05%	-	2.30%	*	1.20%
Physical	Gravity	3.16	2.60	2.60	2.50	*	1.05%	0.56%
	LOI		0.71%	< 1.0%	0.50%	2.80	2.87	2.53
	Specific Surface (BET)	387 m^2/kg	14,200 m^2/kg	20,000 m^2/g	11,000 m^2/g	472 m^2/kg	531 m^2/kg	*
Bogue	C_3S	54%	-	-	-	-	-	-
	C_2S	15%	-	-	-	-	-	-
	C_3A	7%	-	-	-	-	-	-
	C_4AF	9%	-	-	-	-	-	-

* Material data not provided

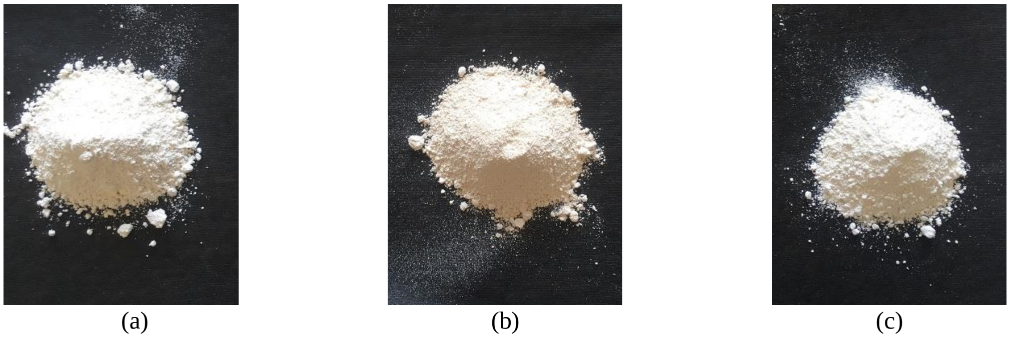

(a) (b) (c)

Figure 6: Small sample of (a) MK1; (b) MK2; (c) MK3

Aggregates conforming to both ASTM C33 and GDOT gradation requirements were used in all concrete and mortar mixtures. The coarse aggregate is a locally sourced from Athens, Georgia, and the fine aggregate is sourced from Watkinsville, Georgia. The coarse aggregate is a standard size #57 (NMAS 1" or 2.54 mm) graded Granite stone. The fine aggregate is an alluvial river sand. Both come from qualified vendors and appear on QPL-1 or QPL-2. Sieve analyses to ensure ASTM and GDOT requirements were conducted (Figures 7-10). Water used for mixing was tap water. Finally, a PCE-based (polycaboxylate ether - BASF's MasterGlenium 7920) superplasticizer was used to lubricate the mixtures (33% solids).

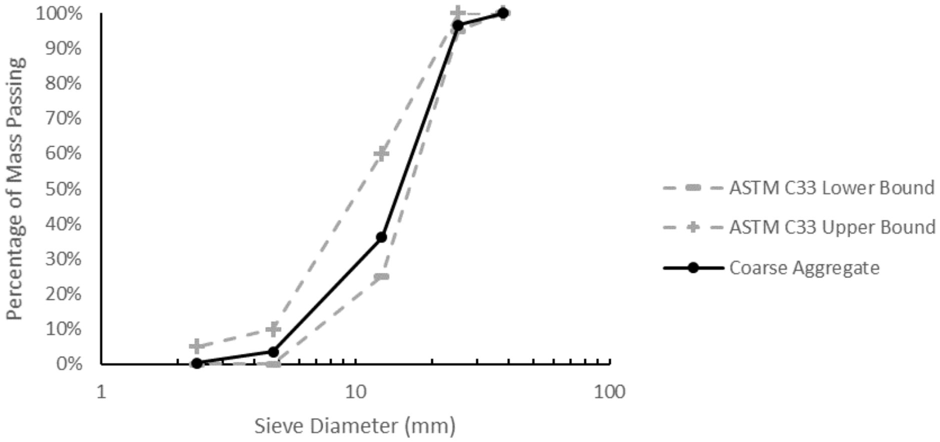


Figure 7: Coarse aggregate sieve analysis with ASTM requirements

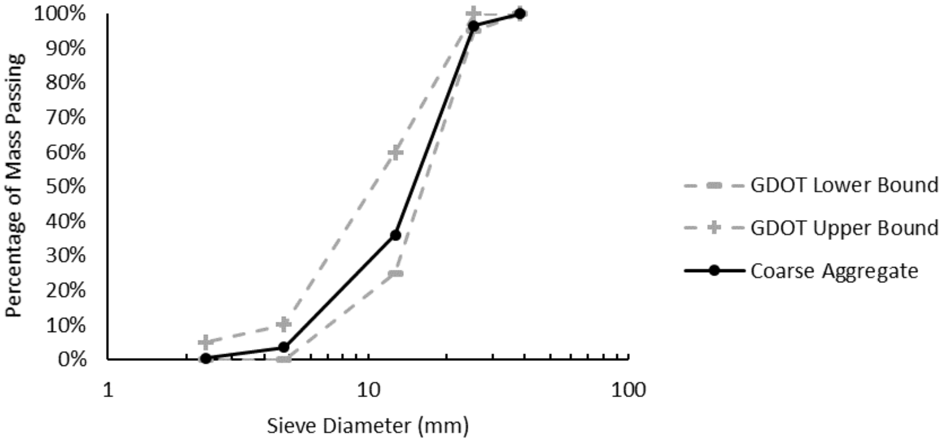


Figure 8: Coarse aggregate sieve analysis with GDOT requirements

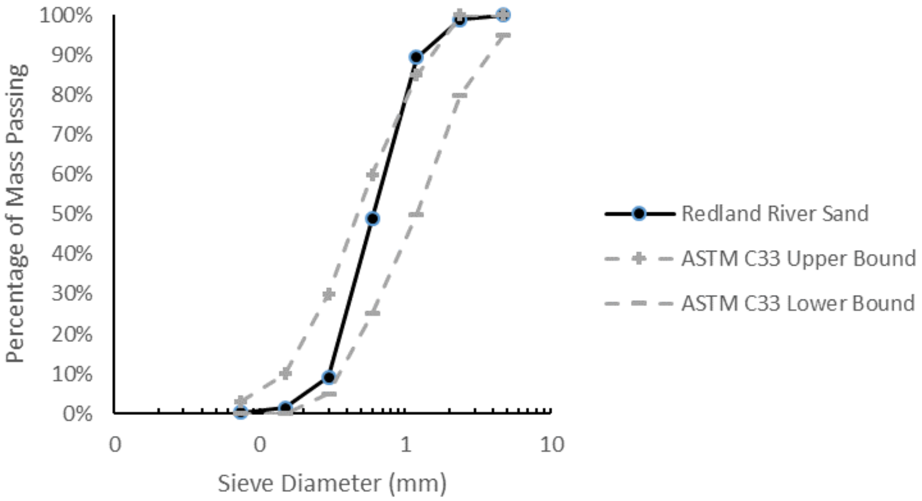


Figure 9: Fine aggregate sieve analysis with ASTM requirements

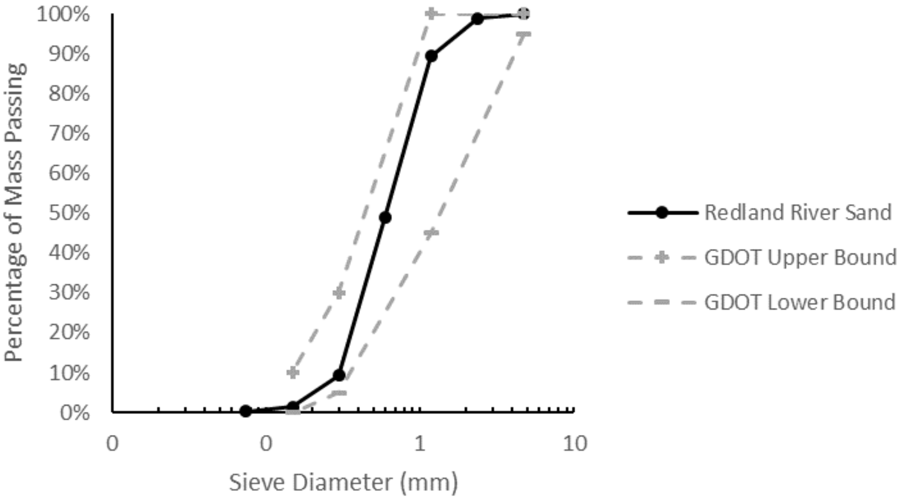


Figure 10: Fine aggregate sieve analysis with GDOT requirements

Mixture Design

Concrete mixture proportions are based on a GDOT drilled shaft design that incorporated a high volume of FA to reduce heat of hydration and cost. The mixture design can be found in Table 6. The total cementitious content for each mixture is 711 pcy (422 kg/m^3). The w/cm ratio is 0.43, and the coarse aggregate fraction is 1,660 pcy (753 kg/m^3). All concrete mixtures incorporate a design air content equal to 4%. SCMs replace a percentage of cement by weight. The weight of sand changed by mixture and was determined according to the absolute volume method as in ACI 211. Saturated surface-dry (SSD) mixture proportions in imperial and SI units can be found in Table 7.

Table 6: Base mixture design

Drilled Shafts Mix - GDOT		
Concrete Strength - 3500 psi (24MPa)	Benchmark Mixture	
	Per cy (m^3)	
Material	Weight	Volume
Cement	391 lb. (177 kg)	1.99 cf
Fly Ash (Class F)	320 lb. (145 kg)	2.23 cf
Coarse Aggregate	1660 lb. (753 kg)	7.37 cf
Fine Aggregate	1210 lb. (572 kg)	10.08 cf
Water	306 lb. (139 kg)	5.06 cf
Entrapped	-	1.00%
BASF Poly 997	10 oz./cwt (6.5 mL / 100 kg cm)	
BASF Poly Z 60	6 oz./cwt (3.9 mL / 100 kg cm)	
BASF Delvo	12 oz./cwt (7.8 mL / 100 kg cm)	

Table 7: SSD mixture proportions per yd^3 (m^3)

Mixture Code	Cement	Metakaolin	Slag	Fly Ash	Coarse Aggregate	Fine Aggregate	Water	Air (%)	Superplasticizer oz./cwt (mL/kg.cm)
Control	711 (422)	-	-	-	1660 (985)	1218 (723)	306 (182)	4%	3.3 (2.2)
MK1-10	640 (380)	71 (42)	-	-	1660 (985)	1205 (715)	306 (182)	4%	6.8 (4.4)
MK1-15	604 (358)	107 (63)	-	-	1660 (985)	1199 (711)	306 (182)	4%	6.7 (4.4)
MK1-20	569 (338)	142 (84)	-	-	1660 (985)	1193 (708)	306 (182)	4%	7.6 (4.9)
MK2-10	640 (380)	71 (42)	-	-	1660 (985)	1205 (715)	306 (182)	4%	6.5 (4.2)
MK2-15	604 (358)	107 (63)	-	-	1660 (985)	1199 (711)	306 (182)	4%	7.1 (4.6)
MK2-20	569 (338)	142 (84)	-	-	1660 (985)	1193 (708)	306 (182)	4%	7.9 (4.1)
MK3-10	640 (380)	71 (42)	-	-	1660 (985)	1205 (715)	306 (182)	4%	6.4 (4.2)
MK3-15	604 (358)	107 (63)	-	-	1660 (985)	1199 (711)	306 (182)	4%	7.5 (4.9)
MK3-20	569 (338)	142 (84)	-	-	1660 (985)	1193 (708)	306 (182)	4%	8.2 (5.3)
SLa-30	498 (295)	-	213 (126)	-	1660 (985)	1202 (713)	306 (182)	4%	3.4 (2.2)
SLb-30	498 (295)	-	213 (126)	-	1660 (985)	1202 (713)	306 (182)	4%	4.1 (2.7)
FA-45	391 (232)	-	-	320 (190)	1660 (985)	1118 (663)	306 (182)	4%	0.8 (0.5)
MK1-15_SLa-30	391 (232)	107 (63)	213 (126)	-	1660 (985)	1183 (702)	306 (182)	4%	7.3 (4.8)
MK2-15_SLa-30	391 (232)	107 (63)	213 (126)	-	1660 (985)	1183 (702)	306 (182)	4%	7.0 (4.6)
MK3-15_SLa-30	391 (232)	107 (63)	213 (126)	-	1660 (985)	1183 (702)	306 (182)	4%	7.0 (4.6)
MK1-15_SLb-30	391 (232)	107 (63)	213 (126)	-	1660 (985)	1183 (702)	306 (182)	4%	7.3 (4.8)
MK2-15_SLb-30	391 (232)	107 (63)	213 (126)	-	1660 (985)	1183 (702)	306 (182)	4%	7.3 (4.8)
MK3-15_SLb-30	391 (232)	107 (63)	213 (126)	-	1660 (985)	1183 (702)	306 (182)	4%	7.0 (4.6)

Mortar mixtures were conducted to make the ASR and sulfate test specimens. The ASTM standards governing 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 7 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 it is specified to alter the w/cm ratio. The choice to deviate from the standard was made because increasing the w/cm ratio has shown to negate the benefits of MK reducing porosity [28]. At SSD conditions of the sand, these mixtures contain the following proportions:

Sulfate mortar bars:

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

ASR mortar bars:

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

Methods

Methods for the batching and testing of concrete and mortar specimens are presented here. Details given in this section are sufficient to reproduce the experiments.

Concrete and Mortar Batching

Concrete mixtures were batched using a Workman II Multimixer portable drum mixer (Figure 11) with a 12.5 ft^3 capacity adhering to 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 2-3 minutes. Once the mixture was visually homogenous the SCMs were added while the mixer continued to rotate. All dry materials were then mixed for approximately 4-5 minutes. The superplasticizer was added to the mixing water and thoroughly agitated before the water was added to the mixer. Finally, after all materials had been added the mixer was allowed to rotate for another 3 minutes, followed by a 2-minute rest period, and then followed by a final 2-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.

Mortar mixtures were batched using a 4.8 L capacity rotating paddle mixer (Figure 12). As with the concrete mixtures, mixture proportions were altered to accommodate deviations from SSD aggregate conditions just prior to batching. Batching of all mortars followed the procedure outlined in ASTM C305. A mixture of portland cement and SCMs were 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.

Stopping the mixer for 90 seconds, the sides of the bowl were scraped down of any clumped material and allowed to mix again for 60 seconds.

Figure 11: Mixer used in concrete batching

Figure 12: Mixer used in mortar batching

Fresh Properties

Concrete temperature, unit weight, air content, and slump were measured directly after batching. A thermometer 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. Temperature and air content were measured to ensure concrete quality, and the unit weight was measured to ensure that MK did not have a significant effect on concrete density. Slumps were measured to understand the extent of workability reduction that is associated with using MK in concrete.

Mechanical Properties

Nine 4”×8” (50mm x 100mm) compression cylinders were made upon each batching; three each for 1-day, 7-day, and 28-day strengths. They were cured in a lime saturated bath (see Figure 13) until the day of testing per ASTM C511. At the age of 1, 7, and 28 days three cylinders were tested in a Forney universal testing machine with a capacity of 800,000 lb. (3.56 MN). Cylinders were loaded at a rate of 440 lb./s (1,957 N/s) until fracture. The average of three specimens was take for each of the three days. An image of a cylinder being tested can be seen in Figure 14.

Figure 13: Lime-saturated curing tank

Figure 14: Fractured compressive specimen

Two tests of tensile strength were performed. The first being 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 (17.2 kPa/s). The average of three was taken as the splitting-tensile strength. Before testing they were cured in a lime saturated bath per ASTM C511. The second test was the modulus of rupture test, which is a test of flexural strength. Three prisms of dimension 6”×6”×22” (150mm×150mm×550mm) were cast at batching and prepared in accordance with ASTM C192. They cured in a lime saturated bath until the age of 28 days, when they were removed and tested in a Forney universal testing machine. The average of three breaks was taken as the MOR (ASTM C78, Figure 15).

Figure 15: Fractured MOR specimen

The dynamic modulus of elasticity (E_d) was performed on 4”x8” (100mm×200mm) cylinders after 28 days of lime curing. The method used the longitudinal resonant frequency to calculate the dynamic modulus, which was obtained by the forced resonance method outlined in ASTM C215. The longitudinal resonant frequency was measured using a Germann instruments DK-5000 dynamic resonance frequency tester. Input parameters included the length, diameter, and weight of the cylinders. Three length and diameter measurements were averaged for the parameters L and d. The equations used for calculating Ed are provided in Equation 4.

$$E_d = DM(n')^2 \qquad \text{(Eq. 4)}$$

Where n' = longitudinal frequency [Hz],

M = mass of specimen [kg],

$D = 5.093\times(L/d^2)$ [m^{-1}]

Durability

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 28 days. They were then pulled out of the bath and the topmost 2” (50 mm) were removed using a diamond-tipped saw. The specimens were then prepped by being subjected to vacuum pressure for 1 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 6 hours per ASTM C1202. Aqueous solutions of NaOH and NaCl were made with concentrations 12g/L of solution and 30g/L of solution, respectively. De-ionized water was used for the solutions. Figure 16 shows the Germann instruments testing equipment used to measure the total charge passed during the test.

Resistance to sulfate attack was measured as specified by ASTM C1012. Six mortar prisms of dimension 1”×1”×11.25” (25mm×25mm×280mm), and six mortar cubes (side dimension 2”, 25mm) were batched and stored at 95°F (35°C) 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 (19.7 MPa). Once the cubes tested above the required strength they were immersed in plastic containers with 0.75 L of aqueous Na_2SO_4 solution per mortar bar. The concentration of Na_2SO_4 was 40g/L of solution. Length measurements were taken at ages of 7, 14, 21, 28, 56, 91, 105, 112, 126, and 168 days after first being immersed in solution. At each of the standard intervals (excluding 126 days) the solution was replaced. Expansion was measured as percentage length change (average of six mortar bars). Figure 17 displays bars in the aqueous solution.

ASR was tested per ASTM C1567. Three mortar bars per mixture were batched to measure expansion by a caustic aqueous solution (40g/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 are 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 immersion into solution.

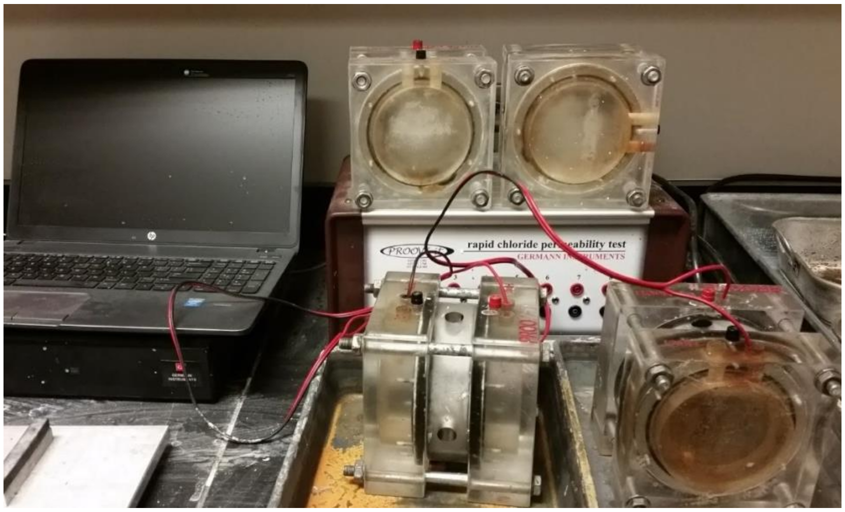


Figure 16: RCPT channels

Figure 17: Mortar bars in sulfate solution

Dimensional Stability

Drying shrinkage was performed in accordance with ASTM C157. Three 4”×4”×11.25” (100mm×100mm×280mm) 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”, 250mm) were calculated and reported as the average percent change of the three prisms.

Figure 18: Drying shrinkage prisms

Figure 19: Length comparator used in sulfate, ASR, and shrinkage tests

The coefficient of thermal expansion was measured for three 4”×7” (50mm×178mm) cylinders after curing for 28 days. The cylinders were cast and cured just as the ones for compression and split-tension. The cylinders were cut to a height of 7” (175mm) using a CC800M CoreCut diamond-tipped saw at an age of 27 days and returned to the curing tank for one additional day of curing before testing. Cylinders were tested two at a time in a Pine Instruments CTE testing machine (Figure 20) for a duration of 18 hours per AASHTO T336. The CTE was taken as the average value of three cylinders.

Figure 20: CTE testing machine

CHAPTER 4

RESULTS

This section contains the results of all experiments discussed in Chapter 3 of this paper. Fresh and hardened properties of all binary and ternary cementitious combinations are included therein.

Fresh Properties

Table 8 shows the fresh concrete properties for all concrete mixtures. Slumps ranged from 1” to 10” (25mm-250mm), and air contents typically ranged from 2.6%-5.5% with a single outlier of 8.5% for MK2-10. Temperatures are relatively within acceptable limits, with two or three nearing upper 80s °F (30°C-32°C).

Table 8: Fresh concrete properties of mixtures in this study

Mixture Code	Slump		Air Content(%)	Unit Weight		Temperature	
	in	mm		pcf	kg/m^3	˚F	˚C
Control	2.5	64	4.1%	146.4	2345	73.0	22.8
MK1-10	8.5	216	5.5%	147.8	2367	75.7	24.3
MK1-15	1.3	32	3.8%	144.4	2313	73.4	23.0
MK1-20	2.0	51	3.6%	143.4	2297	66.6	19.2
MK2-10	3.0	76	8.5%	144.2	2310	82.7	28.2
MK2-15	1.5	38	3.9%	149.8	2399	59.7	15.4
MK2-20	2.0	51	3.6%	144.8	2319	75.2	24.0
MK3-10	6.5	165	3.5%	144.4	2313	78.1	25.6
MK3-15	3.8	95	3.1%	144.0	2307	78.8	26.0
MK3-20	1.5	38	2.6%	144.2	2310	84.6	29.2
SLa-30	1.0	25	4.3%	136.8	2191	68.2	20.1
SLb-30	1.0	25	3.0%	146.8	2351	82.4	28.0
FA-45	6.0	152	0.0%	146.0	2339	86.7	30.4
MK1-15_SLa-30	10.0	254	4.5%	140.6	2252	84.9	29.4
MK2-15_SLa-30	1.8	44	3.9%	141.4	2265	73.9	23.3
MK3-15_SLa-30	9.0	229	4.5%	136.4	2185	75.6	24.2
MK1-15_SLb-30	9.0	229	3.5%	144.6	2316	83.7	28.7
MK2-15_SLb-30	3.8	95	3.8%	143.6	2300	88.2	31.2
MK3-15_SLb-30	2.0	51	5.0%	144.8	2319	80.1	26.7

Binary Metakaolin Hardened Properties

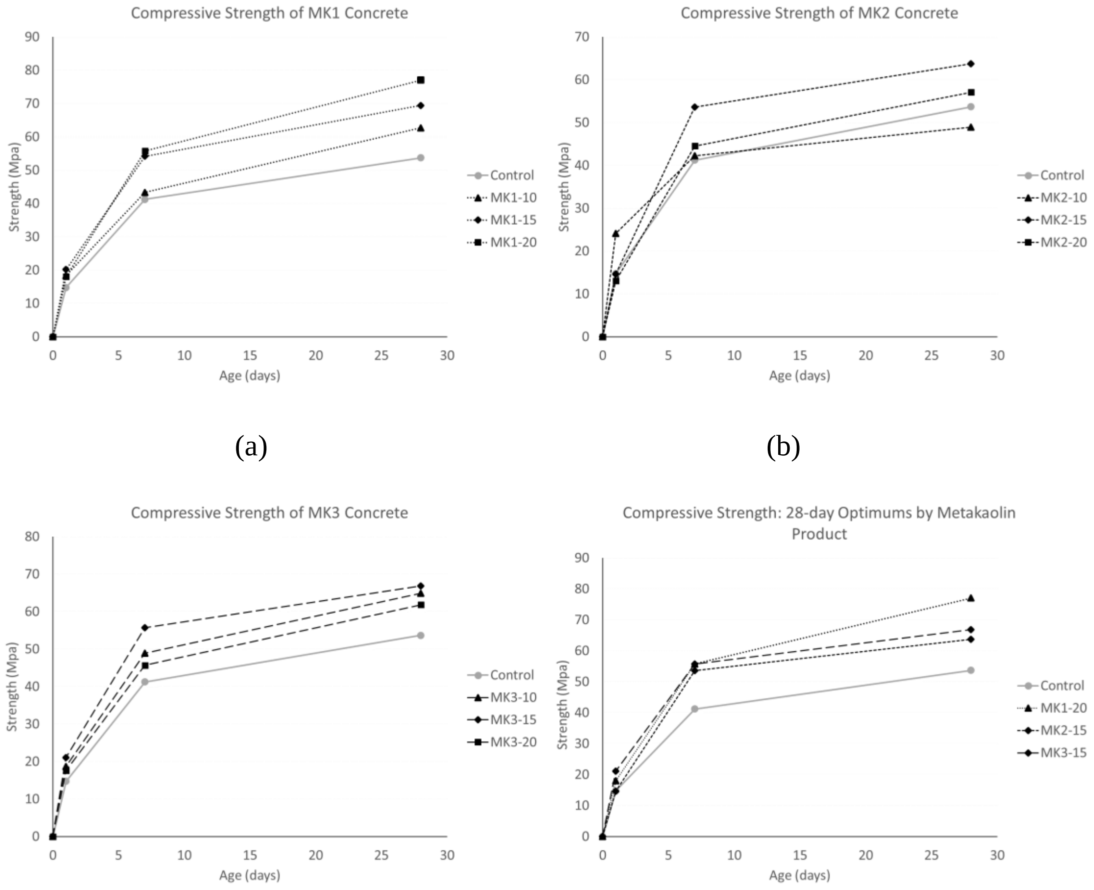
Hardened properties of binary concretes and mortars that contain MK are presented. These include mechanical properties, durability properties, and the dimensional stability of these mixtures.

Mechanical Properties

MK products varied widely in their effect on compressive strength in binary mixtures. MK1 showed a systematic increase in compressive strength with increasing levels of replacement, with the highest compressive strength at 28 days being 11,170 psi (77 MPa) by MK1-20. Compressive strengths over all replacements were 17%-44% higher than control at 28 days. Rates of strength increase from 1-7 days were higher than control for the 15% and 20% replacement levels, and the 1-day strength for all replacement levels were an average of 28% (580 psi or 4 MPa) higher than control. Concretes incorporating MK2 saw an optimum 28-day compressive strength at a replacement of 9,240, 15% (64 MPa, 19%) higher than control. While MK2-20 also saw higher 28-day compressive strengths, MK2-10 saw a 7% reduction in compressive strengths when compared to control and showed a lower rate of strength gain after 1 day of curing when compared to control. However, the 15% and 20% replacement levels saw higher rates of strength gain when compared to control between 1 and 7 days. Overall, strength gains for MK2 ranged from 6%-19%. MK3 performed consistently for all replacement rates, with the highest 28-day strength of 9,700 psi (67 MPa, a 21% increase) contributed to the 15% replacement level. MK3-15 also showed a notable 43% higher compressive strength than control at 1 day of age. Regardless of replacement rate, MK3 showed no lower than a 15% increase in compressive strength over control at 28 days. Overall, only one mixture (MK2-10) did not exhibit a higher 28-day compressive strength than control. These increases range from 6% to 44%. A graphical representation of the compressive strength evolution of the binary MK mixtures can be seen in Figure 21 (a-d).

The split-cylinder tensile strength of the control mixture was 420 psi (2.88 MPa), and the MOR was 710 psi (4.90 MPa). MK1-15 recorded both the highest split-cylinder tensile strength and MOR; 30% and 38% higher than control, respectively. Only one test of tension for MK1, MK1-10, produced a tensile value less than control (10%). Other than this value, MK1 saw increases of split-cylinder tensile strength between 14-30% and increases of MOR between 20%-38%. MK2-20 recorded similar split-cylinder and MOR values to control and decreases in strength for the other two replacement levels were as high as 16% (MK1-15 MOR) when compared to control. All measures of tension for MK3 were the same or higher than control. The optimum replacement level for this MK was 20%, with the split-cylinder tension 13% higher than control, and the MOR being 6% higher. Overall, MK3 saw split-cylinder strength increases between 0%-13%, and MOR increases between 5%-6%. Finally, MK1 saw the most dramatic increases in tensile strength, and indicated a clear optimum replacement level of 15%. However, MK3 saw moderate increases in strength that were consistent among replacement levels. Overall, MK2 caused a reduction in strength. A bar graph comparing the split-cylinder and MOR tensile strengths of the binary MK mixtures can be seen as Figure 22.

The dynamic measures of Young’s modulus of elasticity of the control mixture was 5,440 ksi (37.5 GPa). Decreases across all replacement levels of MK1, MK2, and MK3 were observed, excluding MK 3-10. Decreases ranged from 2%-4% for MK1 concretes, 1%-12% for MK2 concretes, and 0%-9% for MK3 concretes. Figure 23 displays these values by bar chart.



(a) (b)

(c) (d)

Figure 21: Compressive strength evolution for binary metakaolin concretes incorporating (a) MK1; (b) MK2; (c) MK3; as well as the 28-day highest strength mixtures for each metakaolin product (d)

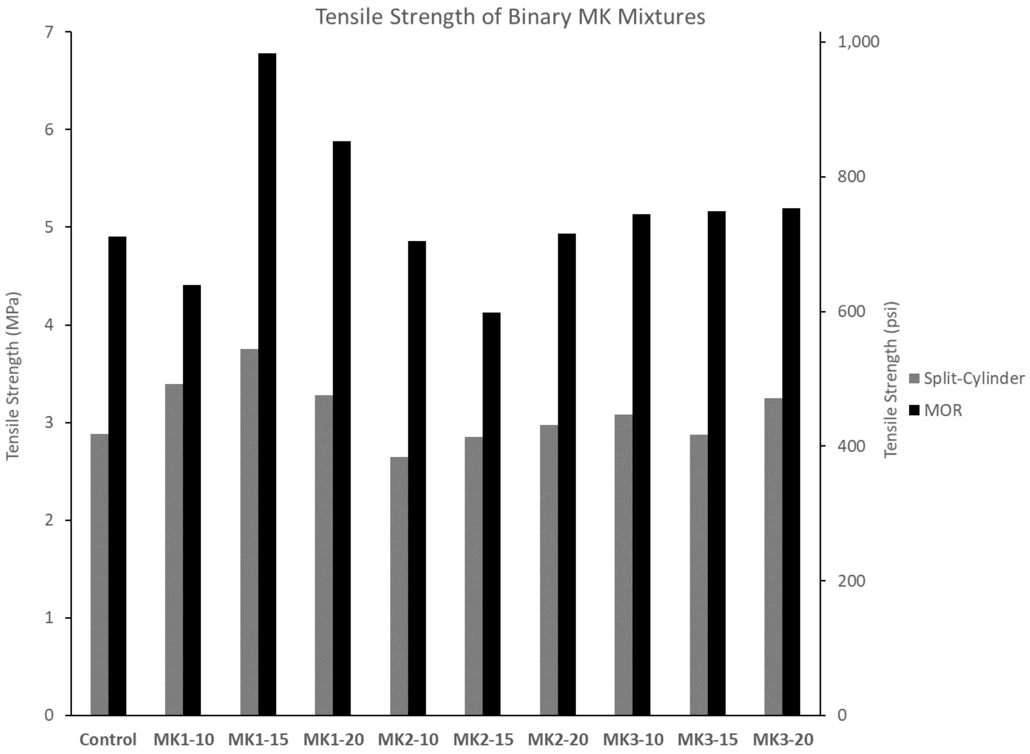


Figure 22: Tension results for binary metakaolin concrete

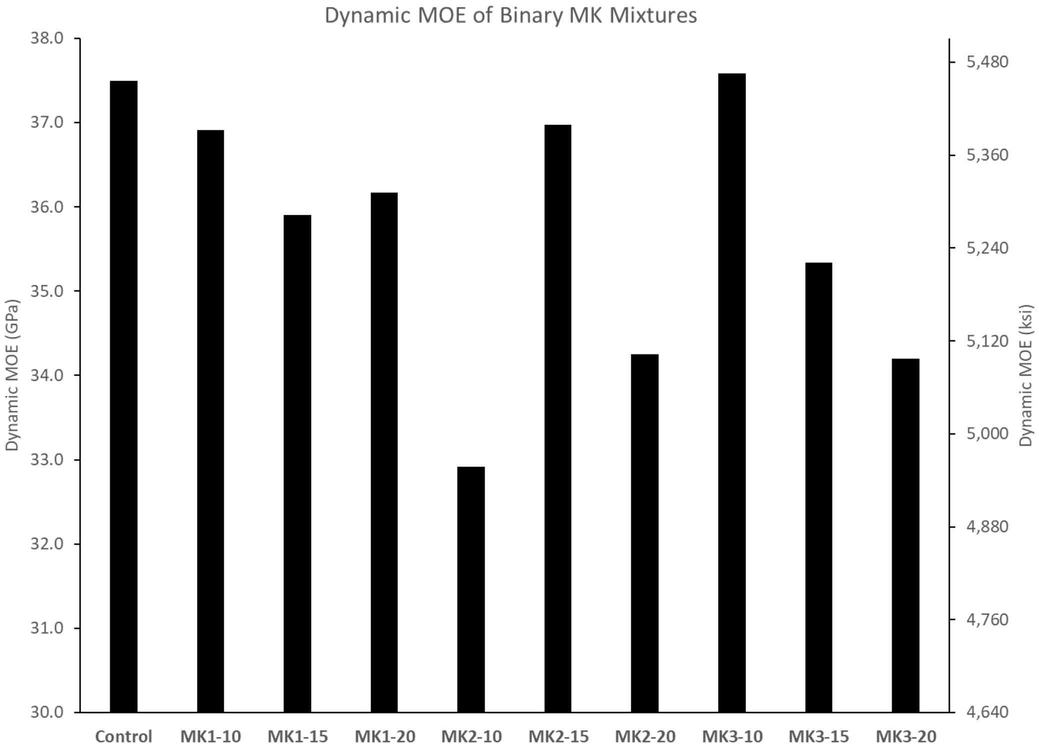


Figure 23: Dynamic MOE for binary metakaolin concrete

Durability

RCPT test indicate that all binary MK mixtures achieved lower permeability to chloride ions than control. All MK1 mixtures belong to the ‘very low’ permeability class (less than 1,000 C passed), with MK1-15 displaying the lowest permeability at 588 C. MK2 required a 15% replacement or greater of cement before reaching the same permeability class, as MK2-10 passed a total of 1,718 C. MK2-15 and MK2-20 passed 693 C and 697 C, respectively. MK3 achieved the lowest permeability, with the lowest being 496 C by MK2-20. However, other MK3 replacement levels performed similarly, with the highest being 712 C. Overall, all MK concretes were classified as having a ‘very low’ permeability, excluding the MK2-10 mixture. Figure 4 provides a visual representation of the RCPT results along with indicators for the permeability classes. It should be noted that MK2-10, while passing the most charge of any binary MK mixture, was classified in a lower permeability class than the control. RCPT results for binary MK mixtures can also be found in Figure 24.

The 6-month (168 days) expansion criterion set in ASTM C 1012 is 0.10% of the original length of the mortar bar. The control mixture exceeded this expansion limit and ended the testing period with a total expansion of 0.47%. All mixtures consisting of a 10% replacement failed to meet the expansion criterion. Most notably, mortar bars for mixtures MK2-10 and MK2-15 deteriorated before they could reach the end of the testing period (91 days and 112 days, respectively). MK2 and MK3 sufficiently limited expansions at replacement levels of 15% and 20%. The systematic increase in sulfate resistance can be seen for increasing replacement levels can be seen in Figure 25.

As previously mentioned, according to ASTM C1567 a SCM combination has sufficiently mitigated expansion due to ASR if it achieves an expansion of less than 0.10% of its original length at the end of the 14-day testing period. The ultimate expansion of the control mixture was 0.17%. A consistent, systematic trend of increased ASR resistivity can be seen as binary MK replacement levels increase. For MK1 and MK2, a 15% replacement level was required to meet this expansion criterion. MK3 was the only MK that was able to meet this criterion at all replacement levels, though MK3-10 expansion was exactly 0.10% at the end of the 14-day testing period. MK1-15 and MK3-15 performed very similarly, with an ultimate expansion of 0.04%. At the 20% replacement level, MK1-20 achieved the lowest ultimate expansion at below 0.02%, while MK3-20 was just over 0.02%. A time history of the expansions can be seen in Figure 26.

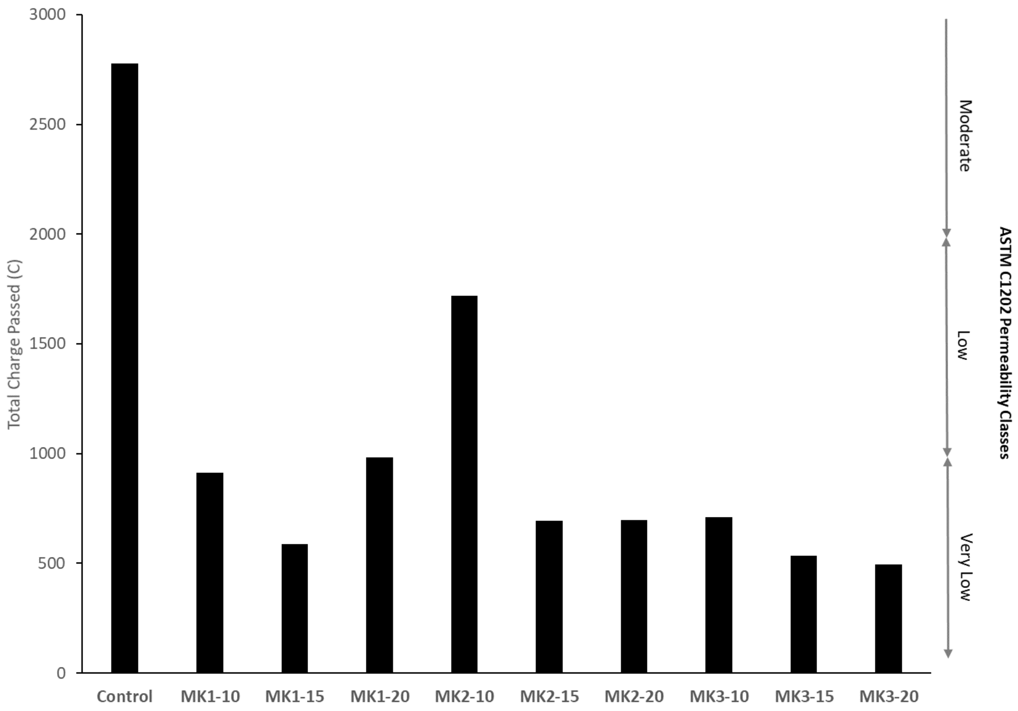


Figure 24: RCPT results for binary metakaolin concrete

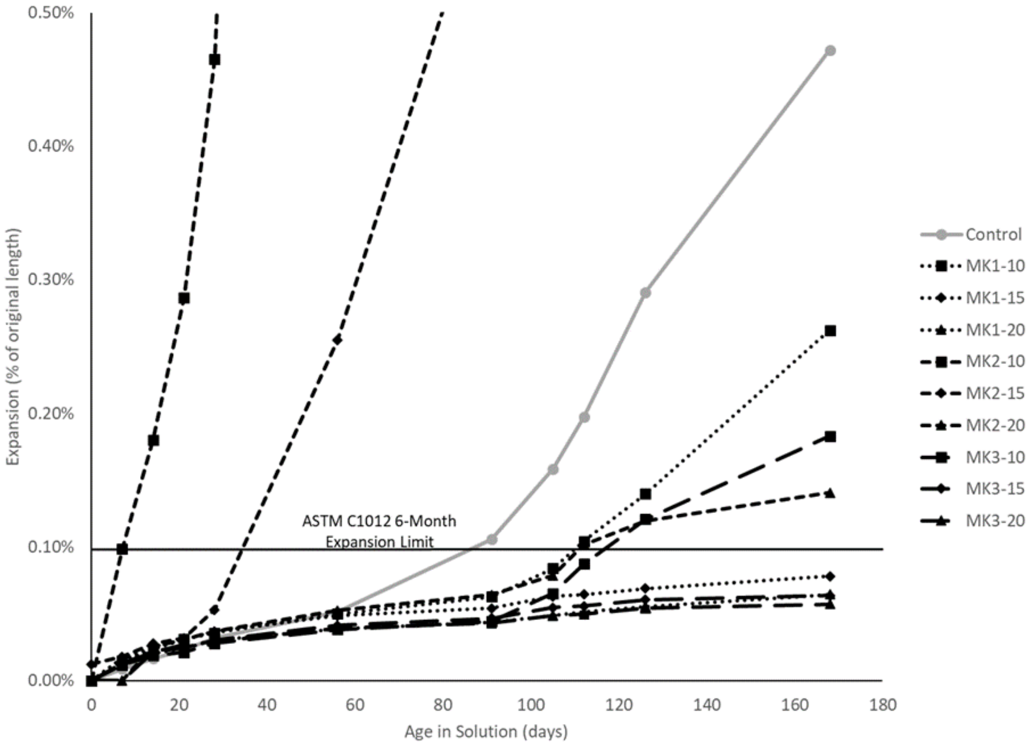


Figure 25: Sulfate expansion of binary metakaolin mortars

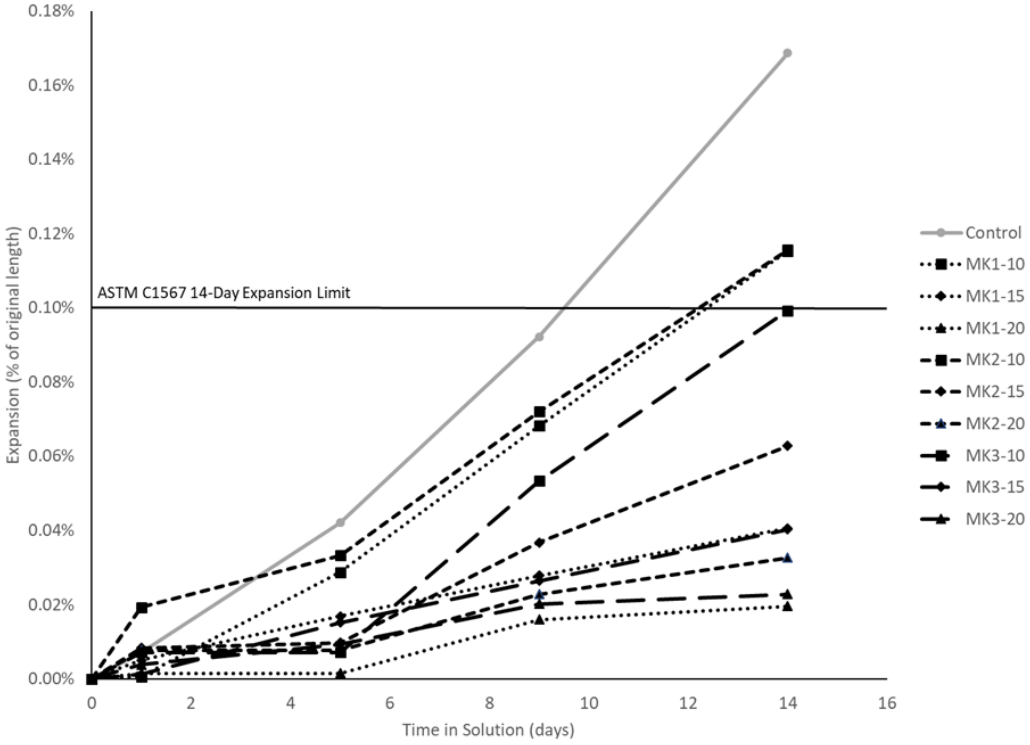


Figure 26: ASR expansion of binary metakaolin mortars

Dimensional Stability

Figure 27 indicates that the ultimate drying shrinkage of binary concretes containing MK were predominantly lower than control. 224-day drying shrinkage of the control mixture was 0.048%. One mixture, MK1-10 was slightly larger at 0.049%. For each product, the overall drying shrinkage decreased systematically with increasing replacement levels. For MK1 these values decreased from 0.049% to 0.039%. For MK2 shrinkage values decreased from 0.045 to 0.039%. Finally, MK3 concrete mixtures decreased from 0.044% to 0.031%, with MK3-20 showing the lowest drying shrinkage in this study.

The CTE of the control mixture was 5.34x10^{-6} in/in/˚F (9.61x10-6 mm/mm/˚C). All binary concrete mixtures containing MK exhibited higher CTEs than control. MK1 saw a high of 5.96x10-6 in/in/˚F (10.72x10-6 mm/mm/˚C) at the 15% replacement level, and a low of 5.53x10-6 in/in/˚F (9.95x10-6 mm/mm/˚C) at 10%. MK2 generally saw lower CTEs than did either MK1 and MK3 and had the lowest binary CTE equaling 9.88x10-6 mm/mm/˚C for MK2-20. Finally, MK3 concretes consistently observed the highest CTEs that ranged from 10.80x10-6 mm/mm/˚C to 11.38x10-6 mm/mm/˚C. MK1 and MK2 exhibited a peak CTE at a 15% replacement, with the 10% and 20% replacements seeing lower CTEs. However, MK3 saw no reduction in CTE from the 15% replacement level to the 20% replacement level. A bar graph of these results can be seen in Figure 28.

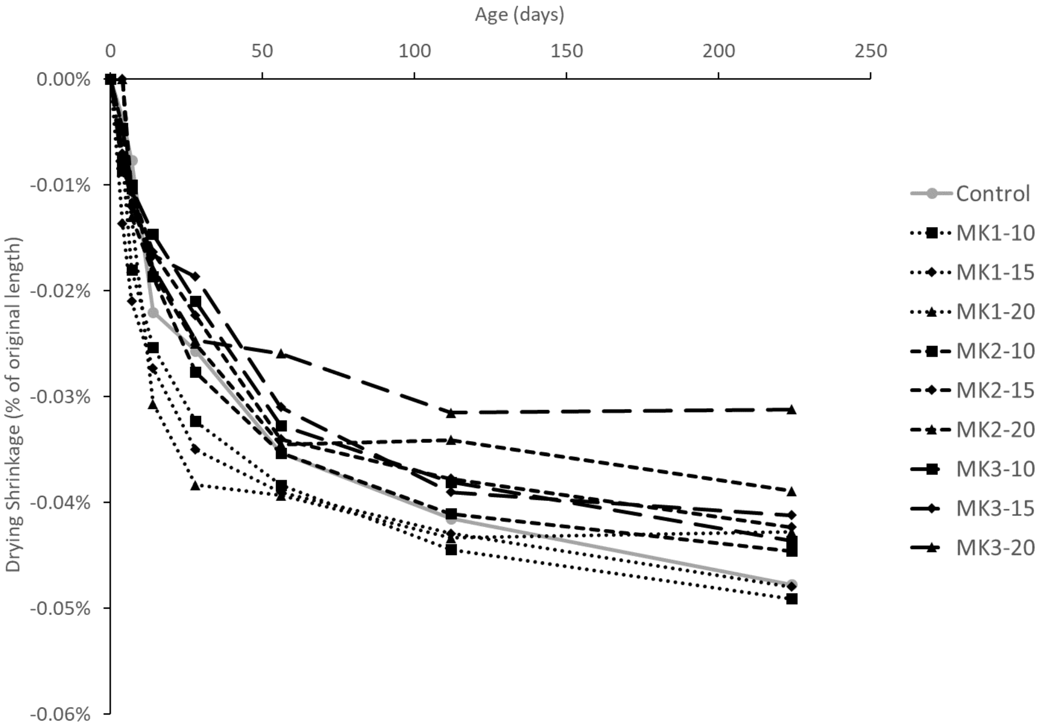


Figure 27: Drying shrinkage of binary metakaolin concrete

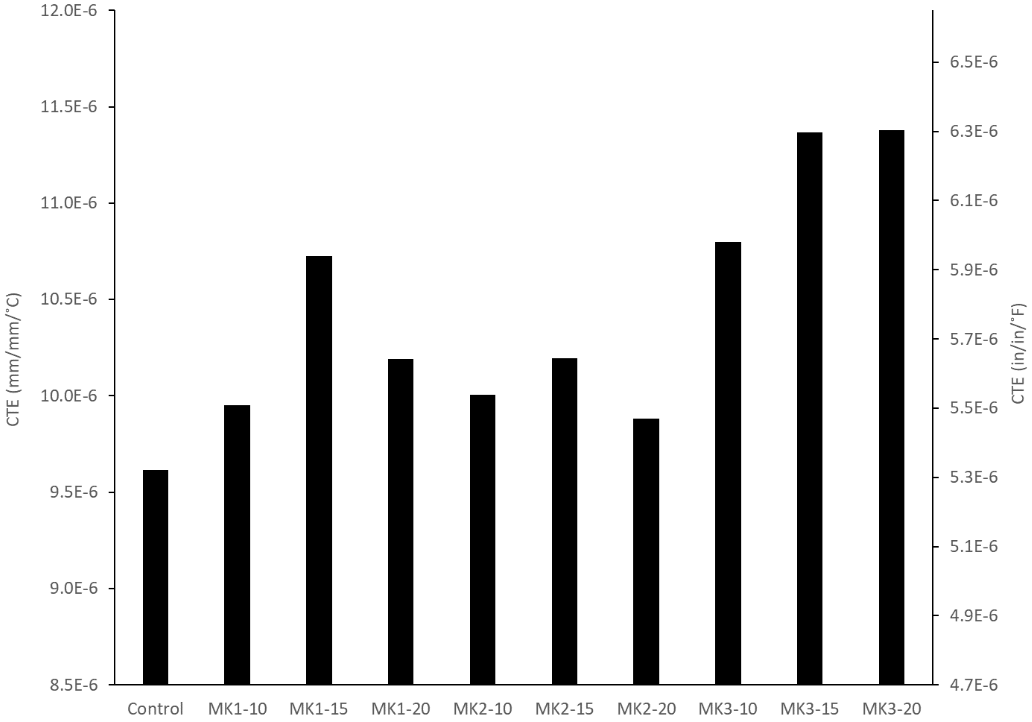


Figure 28: CTEs of binary metakaolin concrete

Ternary and Alternate Binary SCM Hardened Properties

The hardened properties of alternative binary SCM and ternary SCM concretes and mortars are discussed. These include mechanical properties, durability properties, and dimensional stability of these mixtures.

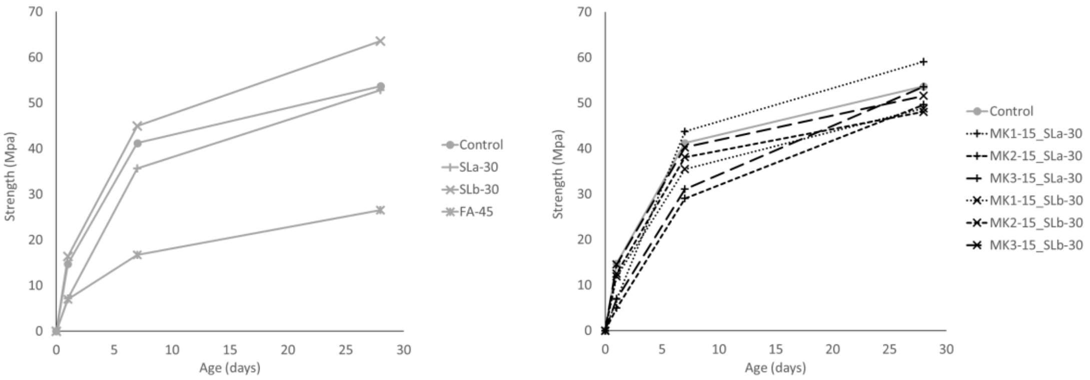
Mechanical Properties

Of the two binary mixtures including slag or FA, only one mixture achieved a 28-day strength higher than control. SLb-20 exhibited a 28-day compressive strength of 9,222 psi (64 MPa), an increase of 18%. Mixtures SLa-30 and FA-45 were 2% and 51% weaker in compression than control, respectively. The rate of strength gain was relatively similar between the two binary slag mixtures, the caveat being that SLb-30 was stronger than SLa-30 by slightly over 1,300 psi (9 MPa) at one day of age. This was nearly the same difference in strength at 28-days of age.

Of the ternary mixtures, only one mixture had a higher 28-day compressive strength than the control. MK1-15_SLa-30 finished with a compressive strength of 8,570 psi (59 MPa), 10% higher than control. MK3-15_SLa-30 finished with a compressive strength very near control, with 7,770 psi (54 MPa). 1-day strengths were similar or less than control for all ternary concretes including SLa. Their compressive strengths ranged from 715 psi – 1010 psi (5 MPa – 7 MPa). Apart from MK1-15_SLa-30, 7-day strengths for concretes including SLa were lower than control as well. However, after an age of 7 days all SLa ternary concretes gained compressive strength at a higher rate than did SLb ternary concretes and the control. By contrast, ternary concretes including SLb did not suffer lower 1-day strengths (1,730 psi – 2,110 psi, 12 MPa – 14.5 MPa), though they were still lower than control. Moreover, ternary concretes including SLb exhibited the highest rate of strength gain from 1-7 days but saw less dramatic strength gain after 7 days of age. Overall (excluding MK1-15_SLa-30) 28-day strengths for ternary concretes ranged from 6,970 psi – 7,769 psi (48 MPa - 54 MPa). Strength evolutions for all mixtures other than binary MK mixtures can be found in Figure 29.

Binary slag mixtures were, overall, stronger in tension than control. Mixture SLa-30 concrete produced a splitting-tensile strength that was 15% lower than control, while SLb-30 was 17% higher than control. MOR values for theses concretes were both higher than control – 740 and 958 psi (5.1 and 6.6 MPa), respectively. The FA mixture saw a strength reduction in splitting-tension and MOR of 24% and 23%, respectively. Ternary SCM concretes typically displayed lower tensile strength than control, however, MK1-15_SLa-30 performed similarly to control for both split-tension and MOR. Furthermore, apart from MK2-15_SLb-30 split tension results, ternary concretes incorporating MK1 and MK3 appear to have higher tensile strengths than do ternary concretes incorporating MK2. Finally, the choice of slag product does not seem to affect the tensile strength of concrete in ternary mixtures. The tensile strength results of binary slag and FA concretes, as well as ternary concretes are found in Figure 30.

Binary slag concretes displayed higher Young's moduli than the control, while all other mixtures saw a reduction from control. Increases were on the order of 150 ksi and 60 ksi (1 GPa and 0.4 GPa) for SLa-30 and SLb-30, respectively. The greatest reduction in the Young's modulus was exhibited by the FA mixture, a decrease of 28% from control. There were no obvious trends among MK or slag products for the ternary concrete mixtures, and reductions in Ed ranged from 12%-22% with an average reduction of 811 ksi (5.6 MPa). Concretes consisting of binary SCM mixtures (non-MK) and ternary SCM mixtures have their modulus values given in Figure 31.



(a) (b)

Figure 29: Compressive strength evolution for (a) alternate binary SCM concrete; (b) ternary SCM concrete

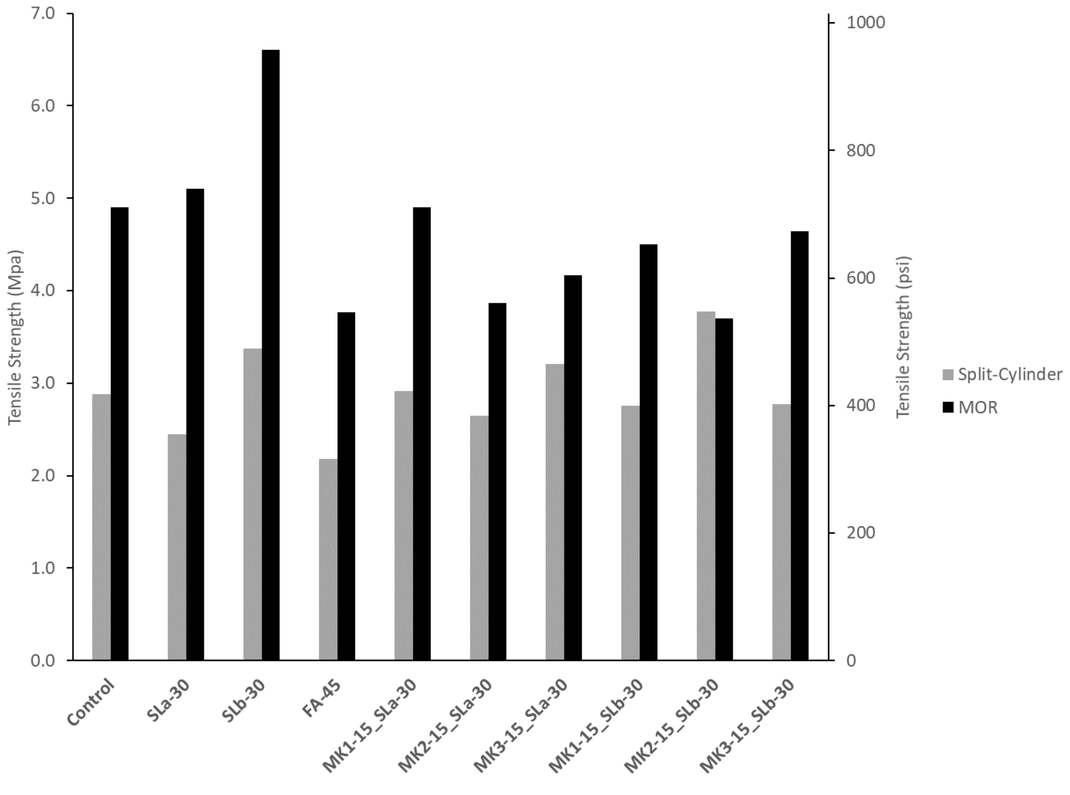


Figure 30: Tensile strength of alternate binary SCM and ternary SCM concrete

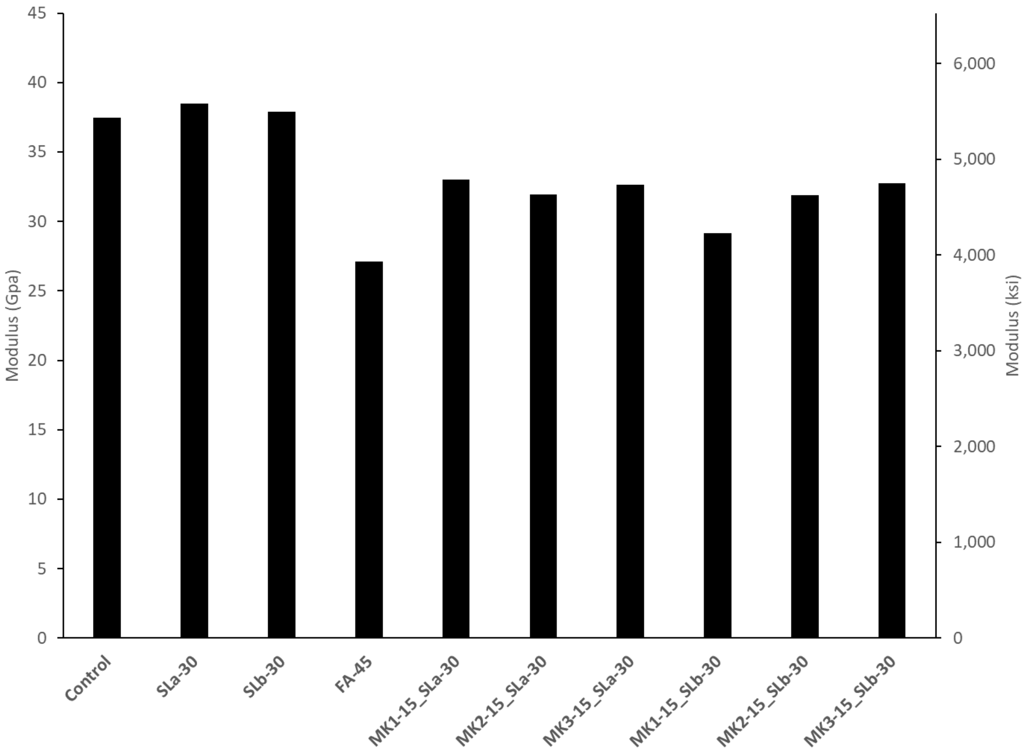


Figure 31: Dynamic MOEs of alternate binary SCM and ternary SCM concrete

Durability

Figure 32 shows that only one of three binary SCM concretes (non-MK) were able to reduce chloride-ion permeability below control. SLa-30 performed similarly to control, while FA-45 almost reached the ‘high’ penetrability classification. SLb-30, however, was effective in reducing the total charge passed to 1,440 C and earning a ‘low’ penetrability classification. All Ternary SCM concretes fell below 1,000 total coulombs passed. Four mixtures were under 500 C. Penetrability classes and results for non-MK binary SCM concretes and ternary SCM concretes can be found in Figure 32.

FA was the only SCM other than MK that was able to sufficiently mitigate mortar expansion for the entire 6-month testing period. In fact, expansion experienced by the binary slag mortars was more accelerated than the control mixture; this was especially so for the mortar incorporating SLa. All ternary mixtures were able to mitigate the sulfate expansion during the 6-month window, and typically resulted in less than 0.06% expansion. Results are presented in Figure 33.

As with the sulfate tests, binary slag mortars at a replacement level of 30% were not sufficient to limit the expansion to below acceptable limits (expansions of 0.11% and 0.12%). The binary FA mortar exhibited similar expansion to the ternary mixtures. All ternary mortars resulted in expansions that were less than 0.03%. Results are presented in Figure 34.

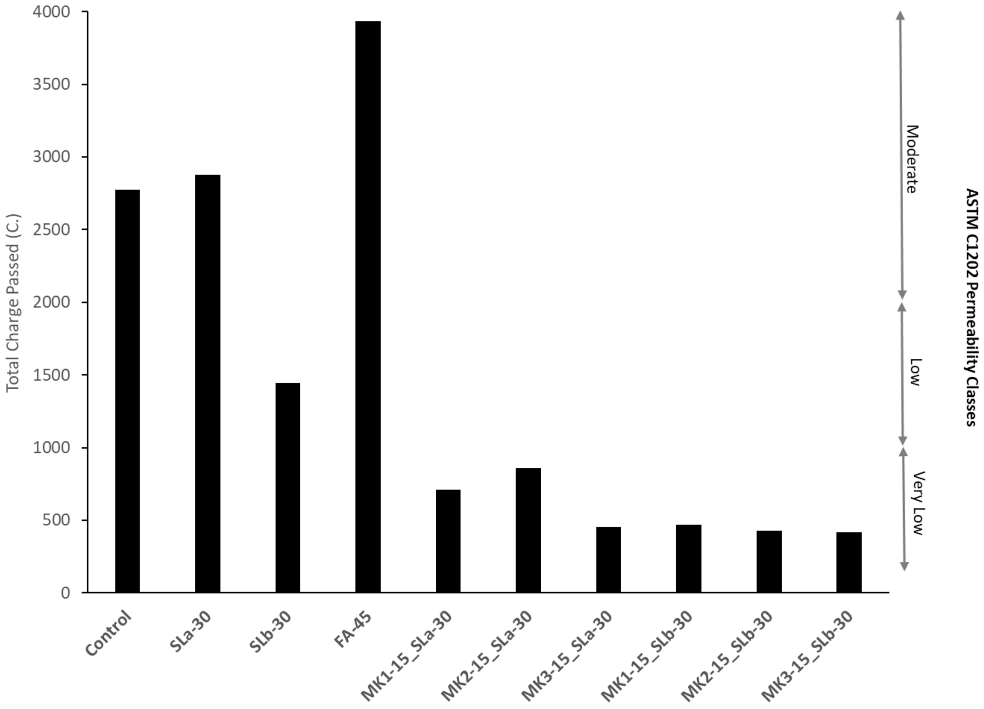


Figure 32: RCPT results for alternate binary SCM and ternary SCM concrete

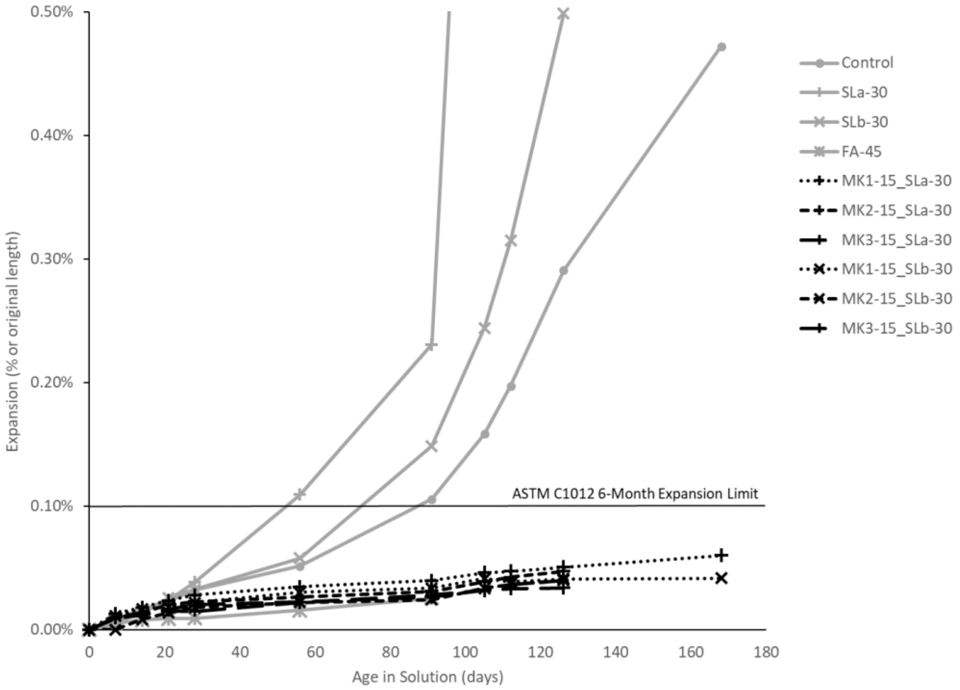


Figure 33: Sulfate expansion of alternate binary SCM and ternary SCM mortars [1]

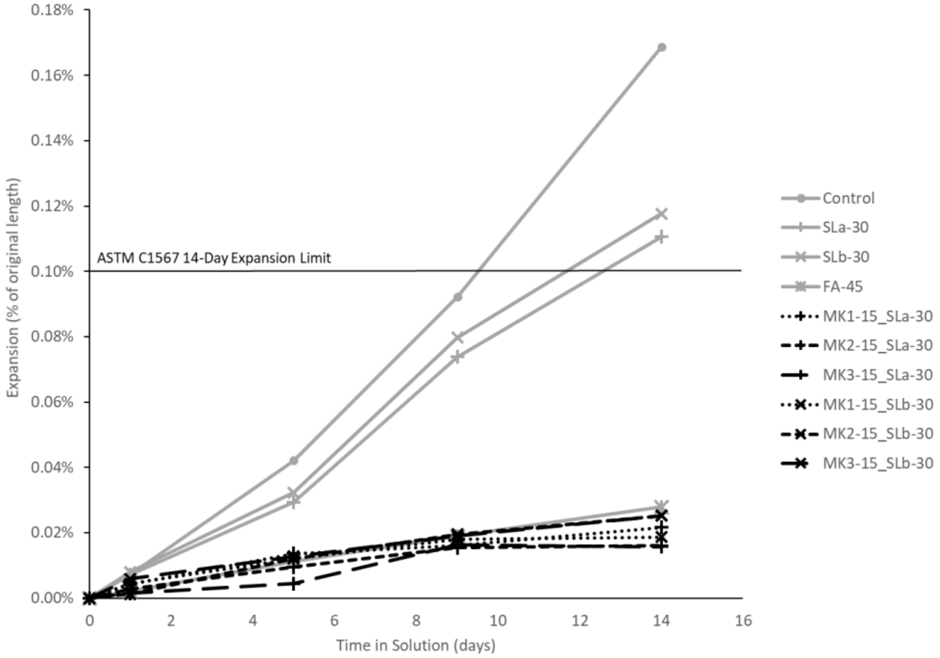


Figure 34: ASR expansion of alternate binary SCM and ternary SCM mortar

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[1] Unfinished results are to be included in journal article.

Dimensional Stability

The binary FA concrete exhibited a 2% lower CTE than control. SLa-30 and SLb-30 varied widely from one another at 3% and 7% higher than control, respectively. The latter was the highest CTE seen outside of the binary MK concretes. MK1-15_SLa-30 saw the lowest CTE in the ternary group with a CTE of 5.40 (9.73x10-6 mm/mm/˚C, an increase of 1% from control). MK2-15_SLb-30 saw the highest CTE in the ternary group with a CTE of 5.70x10-6 in/in/˚F (10.25x10-6 mm/mm/˚C, an increase of 7%). As a group the ternary SCM concretes averaged a CTE of 5.53x10-6 in/in/˚F (9.93x10-6 mm/mm/˚C, an increase of 3%). CTE results are presented in Figure 36.

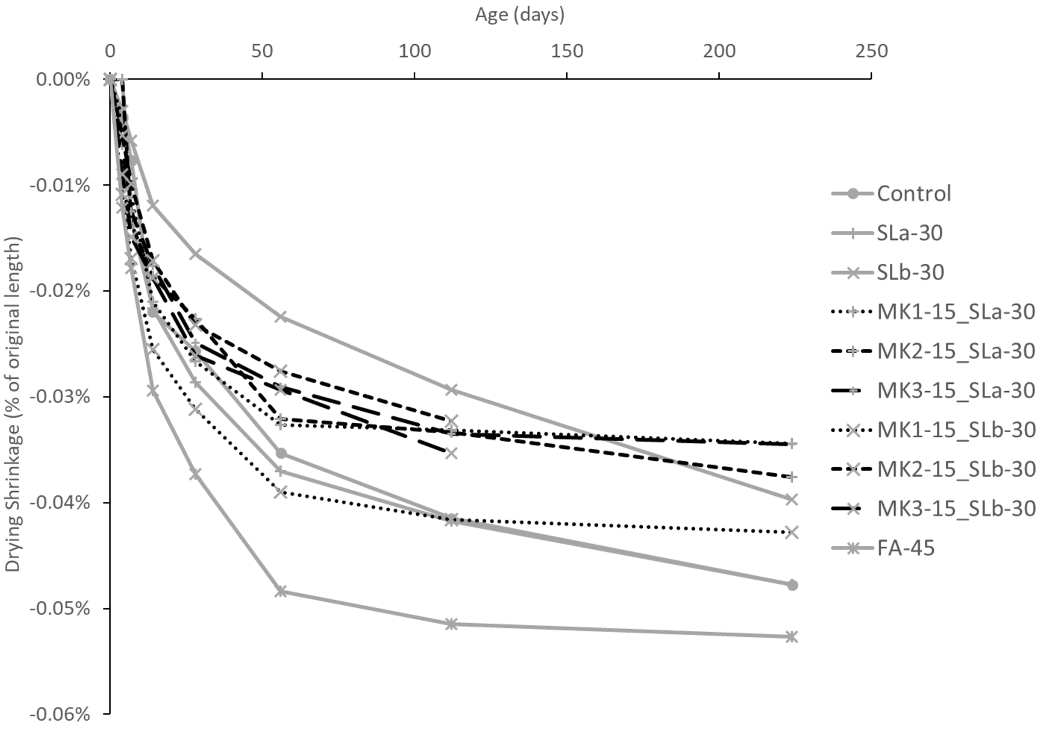

Figure 35: Drying shrinkage of alternate binary SCM and ternary SCM concrete [1]

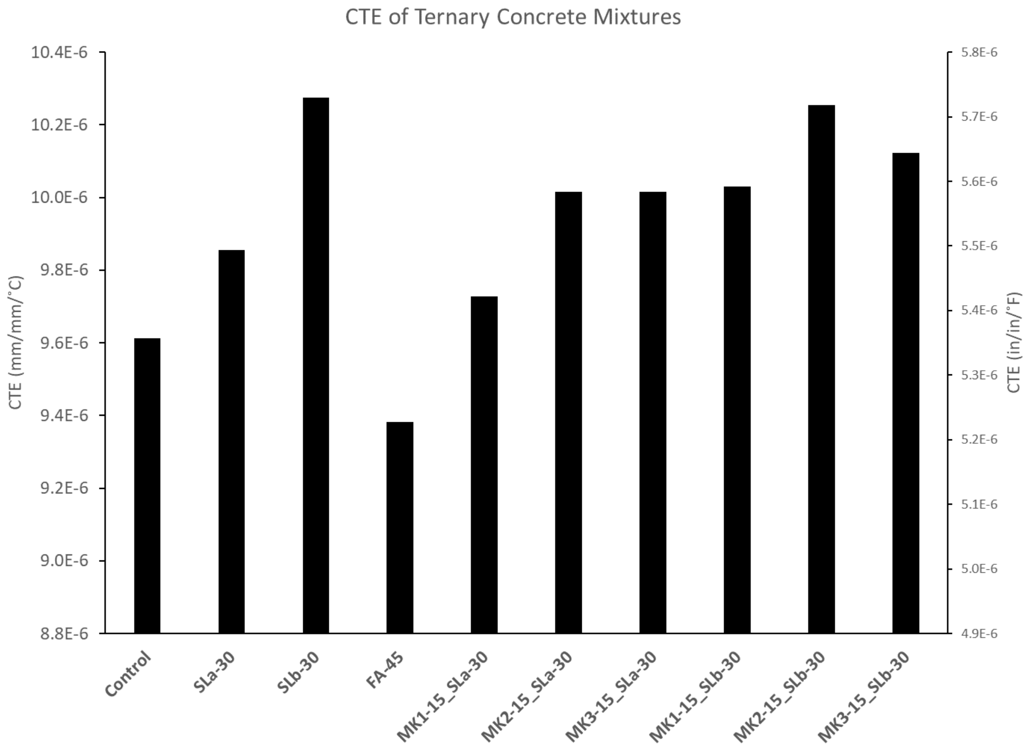

Figure 36: CTEs of alternate binary SCM and ternary SCM concrete

CHAPTER 5

DISCUSSION

This section discusses the results presented in Chapter 4 in the context of existing literature. Binary mixtures including MK will be utilized to discuss important differences between the MK products. The performance of alternative binary SCM and ternary SCM mixtures will be also be discussed.

Comparison of Binary Metakaolin Mixtures

Contrary to expectation, not every MK product benefitted concrete mixtures when part of a binary mixture. In particular, MK2 was inconsistent with respect to its effect on the mechanical strength of concretes. Moreover, a clear difference can be observed between MK2 the other MK products when looking at the durability test results. The expansion of MK2-10 and MK2-15 mortars while in sulfate solution are the most aggressive in the entire testing program. The expansion of MK2-20 while in the sulfate solution most closely resembles the expansion of the other two products' 10% replacement levels. Figure 37 shows disintegration of the MK2-10 mortar bars as a result of deleterious expansion.

With each product, the replacement levels that achieved the highest 28-day compressive strength also achieved the highest 7-day compressive strength. Moreover, the variation was low in these 7-day strengths. Figure 3d shows this tight clustering of 7-day strengths from all products at their 'optimum' replacement levels (54 MPa – 56 MPa). It is worth noting that when these replacement levels were the same (MK2-15 and

MK3-15), the rates of strength gain were very similar at all ages. It is only when the 'optimum' replacement is at 20% (MK1-20) that much higher compressive strength gain is seen after 7 days of age. The tight clustering of the 7-day compressive strength values is considered to be the result of similar oxide composition (Table 7); this is not a poignant statement, as these MKs are being tested specifically because they are commercially-available HRMs ($Al_2O_3 + SiO_2 + Fe_2O_3 \geq 90\%$). However, because the majority of the pozzolanic reaction is completed between 7 and 14 days of age, comparable 7-day compressive strengths may indicate a similar CH consumption and C-S-H formation rates from all MKs when their 'optimum' replacement level is used [25].While this explanation would be consistent with MK1-20 having additional strength gain between 7 and 28 days (additional pozzolanic activity between 7-14 days), it is unknown why MK1 displays a higher 'optimum' replacement level than the other two MKs.

Figure 37: Deleterious expansion by sulfate attack of MK2-10 mortar bars

Trends in the 'optimum' replacement level in compressive strength tests did not translate to the tensile strength results. MK1 saw an optimum tensile strength at a 15% replacement rate, while MK2 and MK3 reached their optimum strengths at a 20% replacement rate. It should be noted that MK1 and MK2 saw much larger variations in their two measures of tensile strength. This is consistent with MK3's compressive strength, in that there was less variation between replacement levels than the other two products. In fact, MK3 mixtures were more consistent across replacement levels than either of the other two MKs in all measures except in the dynamic measure of Young's modulus. Here MK3 saw the largest variation among any MK.

MK1 and MK3 were consistent in their ability to decrease permeability and increase resistance to chemical attacks. The inclusion of these MKs at all replacement levels resulted in very low RCPT permeability classifications, and beyond 15% replacement both products sufficiently mitigated deleterious expansion in aggressive solutions. In addition, MK2 was able to achieve the same permeability classification as the other two MKs at or above a 15% replacement level, and sufficiently mitigate ASR expansion only.

MK2 had the highest fineness of the three MKs, and a similar oxide composition. Increased fineness of MK has been shown to increase the rate of strength gain as well as the overall 28-day strength of concretes [35]. However, the inclusion of MK2 does not result in higher performance across all hardened concrete tests in this study when compared to the other two MKs. Most dramatically, MK2-10 and MK2-15 deteriorated in sulfate solution more than control. Similar performance has only been recorded once in the literature, using a MK with $Al_2O_3 + SiO_2 + Fe_2O_3 = 85\%$ and a loss on ignition (LOI) of 14% [63]. In fact, Table 9 shows that MK2 exhibits significantly less performance for all replacement levels.

Given this information, the following possible explanations of MK2's poor performance are given:

- MK2's high fineness resulted in large agglomerations which were not properly deflocculated during the batching of the concrete.

    - This would explain tensile strengths lower than control, but not the inordinate deterioration of the sulfate mortar bars
- MK2's alumina and silica contents were not amorphous, meaning that an incomplete dehydroxylation of the MK (see [20, 64])
    - This would explain the mechanical performance as well as the rapid destruction of MK2 sulfate mortar bars, as the non-amorphous kaolin would act as inert material
    - For compression and permeability, the inert kaolin would still contribute to particle packing [19], and the alumina content has shown to increase chloride-binding capacity [41, 42]. Moreover, the fine material would still provide additional nucleation sites for cement hydration [25].
    - This does not explain why the optimum replacement level for tensile strengths was 20%

All concretes containing MK exhibit increased expansion due to temperature change, as indicated by increased CTE values from control. Concretes typically achieved a peak CTE value at a 15% replacement. To the knowledge of the author, no research has been published on the CTE values of MK concretes. Research has concluded that the inclusion of FA, slag, and SF reduces the CTE of cement pastes [65]. The mechanism by which the inclusion of SF reduces the CTE is different from that of FA and slag. SF is reported to reduce CTE primarily by reducing the CH contents, which has a higher CTE than that of plain cement pastes. FA and slag are reported to reduce the CTE by CH consumption and increased porosities – as increase in porosity is expected to decrease the CTE. This would support an increase in CTE by inclusion of MK only if the CTE reduction by CH consumption is less than the increase in CTE due to the reduction of porosity. Temporarily ignoring MK2 (poor performance), this explanation is supported by the finer MK (MK1) achieving lower CTE values than MK3, as it is likely that the finer MK exhibits a higher CH consumption with similar porosities (RCPT results). The deleterious results of jointed concrete pavements with CTE values higher than $10x10^{-6}$ mm/mm/˚C have been reported [66].

The reduction in drying shrinkage of concretes by the inclusion of MK is supported by the literature [53-55]. Some researchers have reported a systematic decrease in drying shrinkage with increasing replacement levels of MK [53, 67], while others have reported no observable benefit from higher replacements [54].

Table 9: Summary of binary metakaolin performance

		MK1			**MK2**			**MK3**		
		10%	15%	20%	10%	15%	20%	10%	15%	20%
Mechanical	Compression (28-day)	↑	↑	↑	↓	↑	↑	↑	↑	↑
		17%	29%	44%	-9%	19%	6%	21%	25%	15%
	Split-Cylinder Tension	↑	↑	↑	↓	↓	↑	↑	↔	↑
		18%	30%	14%	-8%	-1%	3%	7%	0%	13%
	MOR	↓	↑	↑	↓	↓	↑	↑	↑	↑
		-10%	38%	20%	-1%	-16%	1%	5%	5%	6%
	E_d	↓	↓	↓	↓	↓	↓	↔	↓	↓
		-2%	-4%	-4%	-12%	-1%	-9%	0%	-6%	-9%
Durability	RCPT Permeability	↓	↓	↓	↓	↓	↓	↓	↓	↓
		-67%	-79%	-65%	-38%	-75%	-75%	-74%	-81%	-81%
	Sulfate Resistance	-	-	-	-	-	-	-	-	-
		F	P	P	F	F	F	F	P	P
	ASR Resistance	-	-	-	-	-	-	-	-	-
		F	P	P	F	P	P	P	P	P
Dimensional Stability	CTE	↑	↑	↑	↑	↑	↑	↑	↑	↑
		4%	12%	6%	4%	6%	3%	12%	18%	18%
	Shrinkage	↑	↔	↓	↓	↓	↓	↓	↓	↓
		3%	0%	-10%	-7%	-11%	-19%	-9%	-15%	-35%

Comparison of Ternary and Alternate Binary SCM Mixtures

Overall ternary mixtures' mechanical strengths were equal to or just below control. Only one mixture, MK1-15_SLa-30, managed to obtain a 28-day compressive strength higher (10%) than control. For comparison, the average compressive strength increase over control for all binary MK mixtures was 18% (ranged from -9% to 44%).

This mixture also had the highest tensile strength of the ternary group, with a MOR equal to that of the control. Although the ternary mixtures out-performed binary concretes incorporating SLa, concretes incorporating SLb saw higher compressive (18% higher than control) and tensile strengths (MOR, 35% higher than control) than all ternary mixtures. Moreover, SLb-30 exhibited the highest tensile strength of all concretes tested.

The early-age strength properties of the ternary mixtures appear to be primarily dependent on the slag product used, with the SLb concrete mixtures recording higher 1-day and 7-day strengths. Ternary mixtures incorporating SLa and SLb exhibit nearly the same strengths as the binary SLa and SLb binary mixtures, respectively. The difference in compressive strengths between concretes incorporating SLa and SLb continue to be visible up to 7 days (Figure 29). After this, all ternary mixtures approach the control compressive strength.

Both MK and slag react pozzolanically with CH in ternary mixtures, which promotes optimum CH consumption and higher paste densities. This is evidenced by the durability results in this paper. However, this does not necessarily ensure higher mechanical strengths, as unreacted SCM is most likely present due to competing pozzolanic activity [60]. This explanation is supported by research that showed that as the level of MK inclusion increased, optimum compressive strengths were found by reducing slag contents [38]. Although slag is also a latent hydraulic material, its CaO content is less than that of OPC, and thus less CH is produced during hydration when slag replaces a portion of cement. In short, in ternary mixtures incorporating 15% MK and 30% slag, the slight reduction in compressive strength is a result of less CH for pozzolanic activity, and more unreacted pozzolan. The increased density of the paste matrix, and additional C-S-H via pozzolanic reactions, compensate for the unreacted material.

The most substantial benefits of the ternary mixtures were seen by the tests of durability, which were most likely the result of high CH consumption. All ternary mixtures indicated very low permeabilities. Five total mixtures passed less than 500 coulombs, and ternary mixtures were 4/5 of these. The ternary mixtures including SLb recorded the lowest permeability, and the most so when combined with MK3 (study low of 419 C). In addition, a sulfate expansion of less than 0.60% was achieved by only one binary mortar mixture (MK1-20). By contrast, five of six ternary mortars finished the 6-month testing period under this value. Similarly, all 6 ternary mortars met ASR expansion criteria. This indicates that, although durability performance varies widely within binary slag and binary MK mortars (see Figures 25-27 and Figures 32-34), ternary mixture durability is consistently high regardless of product combinations.

All ternary concrete mixtures exhibited higher CTE values than the control, however, they were much less those of the binary MK mixtures. As mentioned, increased porosities in FA and slag concrete mixtures have been correlated with decreases in paste CTEs [65]. This is a geometrical property. It is only when high CH consumption exists (using SF), that low-porosity pastes exhibit decreased CTEs from control. This is attributed to the high CTE of CH being replaced by lower CTE C-S-H now being the dominant effect. Figure 32 indicates that ternary concretes incorporating SLa have higher penetrability (and by inference, higher porosities) than SLb concrete mixtures on average. Also, Figure 36 indicates that SLa concrete mixtures exhibit lower CTE values than SLb on average. It is hypothesized that the reduction in porosity lead to higher CTE values in

SLb ternary blends. In ternary blends, the CTE is higher than control but significantly lower than binary MK concretes, which would most likely have lower porosities than ternary concretes. Overall, CTEs of ternary concretes were well below the $10x10^{-6}$ mm/mm/˚C limit for good performance in jointed concrete pavements [66]. Table 10 provides a summary of alternate binary SCM and ternary SCM performance.

Table 10: Summary of alternate binary SCM and ternary SCM performance

		Alternative Binary			**Teranary**					
		FA-45	SLa-30	SLb-30	MK1-15 _SLa-30	MK2-15 _SLa-30	MK3-15 _SLa-30	MK1-15 _SLb-30	MK2-15 _SLb-30	MK3-15 _SLb-30
Mechanical	Compression (28-day)	↓	↓	↑	↑	↓	↔	↓	↓	↓
		-51%	-2%	18%	10%	-8%	0%	-9%	-10%	-4%
	Split-Cylinder Tension	↓	↓	↑	↑	↓	↑	↓	↑	↓
		-24%	-15%	17%	1%	-8%	11%	-4%	31%	-4%
	MOR	↓	↑	↑	↔	↓	↓	↓	↓	↓
		-23%	4%	35%	0%	-21%	-15%	-8%	-25%	-5%
	E_d	↓	↑	↑	↓	↓	↓	↓	↓	↓
		-28%	3%	1%	-12%	-15%	-13%	-22%	-15%	-13%
Durability	RCPT Permeability	↑	↑	↓	↓	↓	↓	↓	↓	↓
		42%	4%	-48%	-74%	-69%	-84%	-83%	-85%	-85%
	Sulfate Resistance	-	-	-	-	-	-	-	-	-
		P	F	F	P	TBD[1]	TBD[1]	P	TBD[1]	TBD[1]
	ASR Resistance	-	-	-	-	-	-	-	-	-
		P	F	F	P	P	P	P	P	P
Dimensional Stability	CTE	↓	↑	↑	↑	↑	↑	↑	↑	↑
		-2%	3%	7%	1%	4%	4%	4%	7%	5%
	Shrinkage	↑	↔	↓	↓	↓	↓	↓	-	-
		10%	0%	-17%	-28%	-21%	-28%	-10%	TBD[1]	TBD[1]

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

This section further adds to the discussion presented in Chapter 5. Important results are summarized, and recommendations are made for the appropriate use of MK in binary and ternary concrete systems. Shortcomings of this study and future work are also presented.

Summary of Findings

Table 9 provides a summary of the performance of binary MK mixtures, while Table 10 provides a similar summary for the performance of alternative binary SCM and ternary SCM mixtures.

The key findings in this study are as follows:

- All concretes incorporating MK as a replacement of cement require a high dosage of superplasticizer ($\geq$ 4 mL/kg of cementitious material or 6.1 oz./cwt), with higher dosage requirements at higher replacement levels by MK.
- Binary usage of MK results in increased mechanical strengths, although the most significant increases are in compression. Increases up to 44% at 28 days of age were seen.
- Binary usage of MK results in increased chloride-ion penetrability and resistance to sulfate and ASR chemical attacks. A replacement level of 15% will ensure adequate resistance, although future work should include ASR tests with reactive aggregates.

- Binary usage of MK resulted in concretes with large CTE values and decreased drying shrinkage. Risk of crack development while using MK will likely depend on type of concrete application (pavement, mass concrete, prestressing, etc.). Time history of CTEs should be studied so that expansion characteristics during hydration can be modeled.
- MK2 was an obvious outlier and did not perform well against sulfate attack. Caution should be exercised in choosing which MK products to put on QPLs. Recommendations will be discussed in the next section.
- Ternary concrete mixtures using MKs and slags (15% MK + 30% slag) tend to perform similarly to one another and control in both compression and tension at 28 days of age. Early-age strength characteristics of the ternary mixtures resemble the early-age strength characteristics of the 30% mixture using the same slag.
- Ternary concrete mixtures using MKs and slags exhibit very high resistance to chemical attack and very low chloride-ion penetrability. All combinations of commercially-available products performed similarly to one another.
- Ternary concrete mixtures using MKs and slags result in increased CTE values, although much lower than binary MK CTEs. Values were near threshold value of $10x10^{-6}$ mm/mm/˚C reported to be deleterious in jointed concrete pavements. Drying shrinkage was lowered from control by these mixtures and was on average lower than the shrinkage of the binary MK mixtures. As with the binary MK mixtures, a time history of the CTEs should be studied if ternary mixtures are to be used in mass concrete. Researchers from this lab have reported the benefits of reduced heats of hydration in these ternary mixtures [62].

Recommendations for Usage

Binary replacements of cement by MK should be used if:

- High mechanical strengths (at any age) are desired.
  - MK provides similar compression benefits to SF [24, 31, 43, 44] but does not suffer from SF's dark coloration.
  - MK is also less expensive than SF, and quality can be ensured because it is not a byproduct.

It is the recommendation of the author that concretes should not incorporate MKs as a binary replacement of cement in massive concreting operations, or in pavements. Figure 28 shows the dramatic effect of some MK products on the CTE. It is the author's opinion that the thermal expansion experienced by these concretes by normal temperature fluctuations would quickly crack and degrade pavements and mass concrete.

Binary mixtures including MK show dramatic benefits in resistance to chemical attack and durability, however, ternary mixtures including slag also see these benefits. If mechanical strengths need only be similar to the control these ternary mixtures it is recommended that a ternary mixture be used. Ternary mixtures see additional benefits above binary MK mixtures:

- Lower CTEs
- Lower heats of hydration [62]
- Increased resistance to chemical attack
- Reduced permeability

Recommended specifications regarding the use of MK include:

- Conforms to ASTM C618

- $Al_2O_3 + SiO_2 + Fe_2O_3 \geq 90\%$ (This ensures that the vast majority of the kaolin base material was kaolinite, not that the majority of the kaolin was converted to glassy alumina and silica. Future study on conversion needed.)
- LOI ≤ 3% by mass
- At least 99% pass through No. 325 sieve
- Strength activity index (ASTM C311) at 7 days of age ≥ 100% (further study needed)
- Replaces a maximum of 20% cement by weight
    - Minimum of 15% if used for ASR or sulfate resistance

<u>Future Work</u>

Further study should evaluate the following:

- The dispersion of high-fineness, plate-like MK in ready-mixed-sized concrete batching. Recommendations are provided by the Silica Fume Association [68].
- The pozzolanic reactivity (ASTM C311) for various commercially-available MKs in the U.S., and its effect on performance of concretes. It is the opinion of the author that the commonly specified minimum of 85% reactivity index (Florida, Texas) is insufficient to ensure quality. Particular attention should be paid to ensure that MKs appearing on QPLs should have a high fraction of kaolinite converted to MK (amorphous, or glassy alumina and silica). Minimum contents should be set by future studies.
- Time-dependent CTEs of ternary mixtures. These mixtures have been shown to reduce the heat of hydration, and low CTEs during hydration period would prove them to be reliable and durable mass concreting mixtures.

- Relationship of MOE by forced resonance method to static MOE measurements of binary and ternary MK concrete

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