

AN ABSTRACT OF THE THESIS OF

Skyler J. Warner for the degree of Master of Science in Civil Engineering presented on March 13, 2012.

Title: The Role of Alumina in the Mitigation of Alkali-Silica Reaction

Abstract approved:

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The use of fly ash as a supplementary cementitious material (SCM) has increased in the last century due to its various environmental benefits as a recycled product. Within the last 60 years, it has been found that it can be used to effectively control damage induced by Alkali-Silica Reaction. However, it is not completely understood how to properly assign a dosage of fly ash to control the reaction. This depends greatly on the fly ash characteristics (e.g. composition, particle size, and reactivity), the reactivity of the aggregate (e.g. high to low reactivity level) and the environmental exposure conditions. The characteristics of the fly ash depend on the coal source being burned and the burning conditions that result in the fly ash formation. A major concern when supplementing cement with fly ash for ASR mitigation is the effect of the alkali contribution of the fly ash to the concrete pore solution. Current test methods cannot accurately determine the alkali contribution of fly ashes and there is no standardized test method to doing so.

When contributed by the implementation of a SCM, alumina has been found to play a role in the ability of an SCM to mitigate ASR-induced damage. It has been observed that fly ashes containing higher levels of alumina (18-25%) tend to improve concrete durability more effectively when compared to fly ashes with lower levels of alumina. Additionally, the use of metakaolin, which is composed of 45-50% alumina, has been found to lessen expansion with a lower percentage of cement replacement than would

be required if fly ash is used. Furthermore, the use of fly ash with another SCM material, a high quality ultra-fine fly ash or alumino-siliceous metakaolin, in ternary blends may improve the performance of fly ash resulting in a broadening of the spectrum of SCMs usable for ASR mitigation.

For successful use of SCMs, it is important to develop an understanding of the alkali-silica reaction and the ability of such SCMs to control expansion. This report provides an overview of alkali-silica reaction and the use of fly ash and metakaolin as SCMs to mitigate expansion due to the reaction, with an emphasis on the role of alumina when contributed from the two materials.

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The Role of Alumina in the Mitigation of Alkali-Silica Reaction

by

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Skyler J. Warner, Author

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Dr. Jason H. Ideker advised on data collection, analysis and interpretation of Chapters 2, and 3.

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1 INTRODUCTION

As the second leading cause of concrete deterioration worldwide next to steel corrosion, alkali-silica reaction (ASR) occurs internally in concrete due to the use of aggregates with reactive silica and a matrix that is rich in hydroxyl ions (e.g. high pH) and alkalis in the pore solution. Additionally, there must be moisture available to drive the reaction that is introduced from either internal or external sources. When these conditions are fulfilled, the alkalis, silica and water combine to form a gel-like material around and within the aggregates as well as within the pores and pre-existing nano/micro-cracks of the concrete. This gel absorbs water molecules when they are available. As the gel absorbs water and expands tensile forces are exerted internally on the concrete which can result in cracking when the tensile capacity of the concrete is exceeded. Surface cracking allows moisture from external sources to more easily penetrate the concrete accelerating the overall rate of reaction and increasing the possibility for other durability concerns.

Damage due to ASR gel expansion may be reduced or possibly eliminated by removing one or more of the three conditions that are deemed necessary for ASR expansion to occur; an adequate amount of alkalis, reactive silica from the aggregates, and available moisture. However, it is likely impossible to completely remove any of these conditions, as mitigation strategies focused on reducing the risk of damaging ASR have been given a great deal of research attention since the 1930s.^{1,2} Mitigation strategies have included the utilization of supplementary cementitious materials (SCMs) that include fly ash, silica fume, ground granulated blast furnace slag, metakaolin, rice husk ash and other natural pozzolans.

The use of fly ash as an SCM has increased in the last century due to its various environmental benefits as a recycled product. Fly ash concrete was first used for the

Hoover Dam in 1929 due primarily to its ability to replace cement as a pozzolanic material and the same strength could be achieved while the internal temperature of the concrete could be greatly reduced.³ Additionally, within the last 60 years, it has been found that it can be used to effectively control ASR-induced damage. However, it is not completely understood how to properly assign a dosage of fly ash to control the reaction. This depends greatly on the fly ash characteristics (e.g. composition, particle size, and reactivity), the reactivity of the aggregate (e.g. high to low reactivity level) and the environmental exposure conditions. The characteristics of the fly ash depend on the coal source being burned and the burning conditions that result in the fly ash formation. A major concern when supplementing cement with fly ash for ASR mitigation is the effect of the alkali contribution of the fly ash to the concrete pore solution. Current test methods cannot accurately determine the alkali contribution of fly ashes and there is no standardized test method to doing so.^{2, 4}

When contributed by the implementation of a SCM, alumina has been found to play a role in the ability of an SCM to mitigate ASR-induced damage. It has been observed that fly ashes containing higher levels of alumina (18-25%) tend to improve concrete durability more effectively when compared to fly ashes with lower levels of alumina.⁵⁻⁹ Additionally, the use of metakaolin, which is composed of 45-50% alumina, has been found to lessen expansion with a lower percentage of cement replacement than would be required if fly ash is used. Furthermore, the use of ternary blends incorporating a high quality ultra-fine fly ash or alumino-siliceous metakaolin may improve the performance of fly ash resulting in a broadening of the spectrum of SCMs usable for ASR mitigation.

For successful use of SCMs, it is important to develop an understanding of the alkali-silica reaction and the ability of such SCMs to control expansion. This thesis provides an overview of alkali-silica reaction and the use of fly ash and metakaolin as SCMs to mitigate expansion due to the reaction, with an emphasis on the role of alumina when contributed from the two materials.

1.1 ASR BACKGROUND

1.1.1 Reaction Basics

Since its discovery in the late 1930s by Thomas Stanton in California, alkali-silica reaction has become a well-known cause of concrete deterioration and is the leading cause of premature concrete deterioration second only to corrosion of reinforcing steel.¹⁰ In the last 10 to 20 years, ASR has become more prominent due to increased alkali contents in cements, higher overall cementitious contents, reduced quantities of available “non-reactive” aggregates and extended service-life of structures. ASR has manifested itself in the form of visible cracks in structures and the loss of service-life of concrete structures.¹¹ In the latter half of the 20th century, cement plants were constructed with kilns with increased capacity. Despite being economically practical, these kilns were subject to degraded venting efficiency. Moreover, driven by government regulation and environmental considerations, there has been a distinct movement towards the recycling of greater proportions of the alkali-abundant dust to the kiln feed. Consequently, there has been a global increase in the alkali content of cement.⁸ Even though the factors that are responsible for deleterious ASR are commonly agreed upon, the process by which the alkali-silica gel causes expansion and consequential cracking in concrete is not entirely understood.

Alkali-silica reaction occurs when the dissolution of alkalis (Na^+ and K^+) produces an increase of hydroxyl ion concentration (OH^-) within the pore solution that catalyze the dissolution of poorly crystalline siliceous materials in fine or coarse aggregates (eg. chert, quartzite, opal, strained quartz crystals). Despite representing a small component of portland cement (typically 0.20 to 1.30% $\text{Na}_2\text{O}_{\text{eq}}$ for cements of North America),

alkalis dominate the pore solution, which essentially becomes a mixed solution of NaOH and KOH.¹

When subjected to such a strong alkaline solution, an acid-base reaction occurs between the acidic silanol (Si-OH) groups of the poorly-crystalline hydrous silica and surrounding hydroxyl ions in solution. As the reaction proceeds leading to further penetration of hydroxyl ions into the silicate structure, some of the siloxane linkages (Si-O-Si) are also attacked. These two reactions occur as follows:^{1, 12}



and



The alkali-silica gel is formed when this separation of silica is concurrently charge balanced by the alkalis left behind in solution when the abundance of hydroxyl ions was created.¹ In a solution of alkalis and silica coupled with the absence of calcium the two species would remain in solution.¹³ However, ample amounts of Ca(OH)_2 exist, especially in plain or neat portland cement concrete, that results in the initial reaction product for alkali-silica gel comprised of minor amounts of CaO. This alkali-silica gel is hygroscopic and has the affinity to imbibe water from nearby pore solution, an action that results in expansion of the gel that may be present in preexisting cracks and voids as well as within and around aggregate particles. As the calcium content of the gel increases, a portion of the alkalis are released back into the pore solution resulting in a recycling effect of the components required for ASR gel creation and expansion.^{1, 14, 15}

Continued expansion and an ensuing increase of internal tensile stress may cause further cracking of the aggregates, cement paste, and overall cement matrix. ASR causes characteristic ‘map cracking’ in unrestrained concrete (containing no reinforcement) and cracking is aligned with the primary reinforcement in reinforced structures (as movement can only occur in the perpendicular direction to restraint). As discussed, it has become widely accepted that there are three necessary ingredients for alkali-silica reaction to cause such damage in concrete: sufficient alkalis, reactive silica, and adequate moisture.

1.1.1.1 Alkalis

In general, the portland cement provides the **alkalis** (in this case Na^+ and K^+) that contribute to alkali-silica gel formation. However, additional alkalis can also be contributed by supplementary cementing materials (SCMs), chemical admixtures, and external sources such as seawater or deicing salts/chemicals. Alkalis can also be contributed by certain aggregate species, such as those that contain feldspars.¹⁶

The sodium oxide equivalency in the portland cement is determined by Equation 3:

$$\text{Na}_2\text{O}_{\text{eq}} = \text{Na}_2\text{O} + 0.658 \text{ K}_2\text{O} \quad [\text{Equation 3}]$$

Where: $\text{Na}_2\text{O}_{\text{eq}}$ = the total sodium oxide equivalent, in percent by mass

Na_2O = sodium oxide content, in percent by mass

K_2O = potassium oxide content, in percent by mass

The concentration of alkalis in portland cement commonly ranges between 0.2 to 1.3 percent. This can be comparatively low to the other oxides in portland cement. Initial

research on ASR proposed that when the percentages of alkalis in the cement fell below 0.6 percent $\text{Na}_2\text{O}_{\text{eq}}$ expansion due to ASR was unlikely to occur.¹⁰ Although used as a mitigation option to limit ASR, reducing the percent contribution of alkalis from portland cement is not an effective method of mitigating ASR for all reactive aggregate types when used solitarily. This is because the total alkali content (or alkali loading) of the concrete does not result in being limited.¹⁶ Any alkalis present disassociate in the pore solution leaving K^+ and Na^+ that must be charge balanced in order to create equilibrium by the transfer of hydroxyl ions from the concrete matrix. The presence of hydroxyl ions raises the pH of the pore solution. The reduction in the pH and the alkalinity of pore solutions correlate well with observed reduction in expansion of concrete prisms and mortar bars.¹⁷ The pH acts as a trigger for ASR, which is activated when it reaches between 13.2 and 13.8.^{16, 18}

1.1.1.2 Reactive Silica

Reactive silica is non-crystalline (amorphous) or disordered silica and found in many common aggregates. Aggregates that contain a poorly crystalline silica structure have an increased susceptibility to ASR due to its increased solubility; thus amorphous silica will dissolve more readily in the high pH of the pore solution of concrete. The expansion due to ASR, in some cases, can increase in proportion to the amount of reactive aggregate in the concrete. Conversely, some aggregates display a pessimum effect where if the proportion of reactive aggregate in test mixes is varied, while other factors are kept constant, maximum concrete expansion occurs at a particular aggregate content. In essence this represents an ideal ratio of reactive silica to available alkali that will produce the highest expansion level due to deleterious ASR. Therefore it is important to perform laboratory testing to determine mixture specifics that may be

altered to reduce the potential for ASR. The mineralogy of the aggregate, crystallinity of the silica and its solubility all play a role in the degree of reactivity of aggregates.¹⁹

1.1.1.3 Adequate Moisture

Once the alkali-silica gel has formed, **adequate moisture** is the final necessary component for deleterious ASR and expansion of the gel to take place. Water can be contributed from within the pore solution of the concrete or from external sources. It has been established that for prolonged expansion of the alkali-silica gel a minimum internal relative humidity of 80 percent is required.^{16, 20}

1.1.1.4 Alkali-Silica Reaction and the Mechanism of Gel Formation

The name alkali-silica reaction can be deceptive considering the first actual reaction takes place between the hydroxyl ions (OH^-) in the pore solution that exist near the surface of reactive siliceous aggregate. Due to the charge balance and equilibrium effect, the elevated concentration of the hydroxyl ions and alkali cations is equivalent. This elevated OH^- concentration due to the formation of hydration products results in an increased pH that concurrently results in the dissolution of silica from the reactive siliceous aggregate.¹⁶ The interaction between the hydroxyl ions and surface of the siliceous aggregate produces silanol (Si-OH) groups, as depicted by Equation 4. As the concentration of OH^- ions increases, a penetration of the aggregate occurs and silanol groups are dissolved into SiO^- molecules, as depicted by Equation 5. Present in the interfacial transition zone (ITZ), near the surface of the aggregate, the SiO^- molecules draw positive cations due to charge balance equilibrium (Na^+ and K^+) from the pore solution and form Si-O-Na , as depicted in Equation 6.^{16, 21} Although Equations 4-6 involve sodium (Na) as a cation for modern concrete it is the potassium (K) that is dominant.



The resulting Si-O-Na material constitutes the alkali-silica gel that accumulates at the ITZ and proliferates around the surface of the aggregate and through existing cracks adjacent to the aggregate. The alkalinity of the pore solution, reactivity of the silica in the aggregate, and availability of moisture affect the overall rate and amount of gel formation and expansion.¹⁶

1.1.1.5 Role of Calcium in Alkali-Silica Reaction

Hydration, the chemical process of combining the cementing materials and water, results in the formation of calcium hydroxide (CH) and calcium silicate hydrates (C-S-H), as well as other hydration products (ettringite, monosulfate, etc.). The calcium from the formation of these products (especially CH) can have an effect on the rate and amount of alkali silica gel formed. Research carried out by Thomas and co-workers concluded that significant expansion only occurs when an adequate supply of calcium is available as calcium hydroxide, thus confirming that calcium is required to promote expansion due to ASR.²¹ Thomas et al. carried out a number of experimental studies comparing cementitious systems upon which calcium was available in various forms and concentrations. The results concluded that systems without calcium hydroxide (CH) showed very little expansion, and the pore solution analysis of these systems determined that the released silica from aggregates remained in solution as opposed to reacting to form ASR gel.²¹ Although the role calcium plays on gel expansion remains unclear, a series of mechanisms have been proposed, as listed below:

- Calcium may replace alkalis in the reaction product thereby regenerating alkalis into the pore solution for further reaction (alkali recycling)^{21, 22}
- CH may act as a buffer maintaining a high level of OH⁻ in solution^{21, 23}
- High calcium concentrations in the pore solution prevent the diffusion of silica away from reacting aggregate particles^{21, 24, 25}
- If calcium is not available, reactive silica may merely dissolve in alkali hydroxide solution without causing damage^{21, 26}
- The formation of calcium-rich gels is necessary to cause expansion either directly or through the formation of a semi-permeable membrane around reactive aggregate particles^{21, 27, 28}
- Therefore, promoting the formation of C-S-H at the expense of calcium hydroxide may result in successful mitigation of expansion due to ASR. In addition, C-S-H can be effective in binding alkalis, further improving the resistance of concrete to deleterious ASR.^{2, 5, 29, 30}

Therefore, promoting the formation of C-S-H at the expense of calcium hydroxide may result in successful mitigation of expansion due to ASR. In addition, C-S-H can be effective in binding alkalis, further improving the resistance of concrete to deleterious ASR.^{6, 31}

1.1.2 Mechanisms of Gel Expansion

While the mechanisms behind ASR gel formation are well understood, the actual mechanism for expansion remains uncertain. Four theories, which have emerged since the 1930s, are in mutual agreement that the main component driving the mechanism of gel expansion is water. These four theories are named the double-layer, osmotic pressure, CSH-shell, and the calcium/alkali exchange theory.

1.1.2.1 Osmotic Pressure Theory

The osmotic pressure theory suggests that the cement paste surrounding the reactive aggregates blocks large silicate ions from exiting while allowing the water and alkali hydroxides to diffuse through. The resulting alkali silicate formed draws solution through the cement paste forming more alkali silicate gel. The gel swells creating an osmotic pressure cell and increasing internal hydrostatic pressure that results in cracking.¹⁴

1.1.2.2 C-S-H Shell Theory

The C-S-H shell theory hypothesizes that in the presence of calcium hydroxide, alkali ions and hydroxyl ions enter into the aggregate matrix of reactive silica leaving calcium and anions in the pore solution. As hydroxyl and alkali ions penetrate, a breakdown of the Si-O-Si bonds occurs allowing for further penetration of ions and the release of SiO₂ into the pore. When concentrations of Ca(OH)₂ and alkali salts in the pore solution are high, the diffusion on SiO₂ becomes restricted while materials continue to penetrate the aggregate structure. An expansive force is generated within the aggregate by this disparity.³²

1.1.2.3 Calcium/Alkali Exchange Theory

The calcium/alkali exchange theory hypothesizes that the gel adsorbs Ca²⁺ ions in exchange for alkali ions that react with the surrounding pore solution to create additional alkali-silica gel. The resulting gel occupies more space and generates expansive forces that produce cracking.³³

1.1.2.4 Double-Layer Theory

The double-layer theory suggests that gel expansion is caused by electrical double-layer repulsive forces. The interaction of a liquid and a solid causes the solid surface to carry excess charge electrifying the region. The interaction of the highly-charged silica aggregate surface with the alkaline pore solution of the concrete leads to the breakdown of the silica and the formation of the alkali-silica gel. Within the gel, a “rigid layer” is formed around the solid particle due to the binding of negatively charged solid silica particles and positively charged cations. A “diffuse layer” surrounds this rigid layer consists of more cations and anions found within the gel.³⁴ This electrical double layer (composed of sodium, potassium, and calcium ions surrounding a negatively charged silica surface) takes in water causing the size of the external layer to increase around the particle. Electrostatic forces eventually predominate and particles are pushed apart as the gel increases.^{35, 36}

Though no single theory is widely agreed upon, it is commonly understood and supported that water is the primary driving force for expansion of alkali-silica gel. None of the theories discussed above consider the role of short-range forces which could play a crucial part in the expansion process. Also, neither the osmotic pressure theory nor the double-layer theory considers the potential effect of calcium. Therefore, current theories explaining the expansion of alkali-silica gel may be inaccurate and thus it remains unknown exactly how the gel expands in concrete. This said, portions of the theories described above may together explain the mechanism behind alkali-silica gel expansion or lead to a more complete explanation.

1.1.3 Test Methods for Alkali-Silica Reaction

Since ASR was first discovered, a variety of test methods to detect the reactivity of aggregates have been developed. Modifications to these test methods have also been created for testing the efficiency of mitigation materials such as supplementary cement materials and/or chemical admixtures. It is important to draw attention to the methodologies responsible for providing the most accurate and reliable results to determine which will be used during the current research project for detecting aggregate reactivity and determining the most effective mitigation practices. ASTM International and Canadian Standards Association (CSA) standards provide detailed descriptions of their recommended test methods and expansion limits, as displayed in Table 1-1. The ASTM methods will be followed in this research project unless otherwise stated and a brief description of those used follows the table.

Table 1-1: Recommended test methods according to ASTM and CSA standards.

Petrographic Examination			
ASTM Test Method	CSA Companion	Description	
ASTM C 295: Standard Guide for Petrographic Examination of Aggregates for Concrete	CSA A23.2-15A: Petrographic Examination of Aggregates	Guide to classify and quantify potentially reactive mineral phases in aggregate, the constituents of the sample, determine physical and chemical characteristics, and compare samples of the aggregate with other sources for which test data and performance records are available.	
Mortar Tests			
ASTM Test Method	CSA Companion	Description	Expansion Limits
ASTM C 1260-07: Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)	CSA A23.2-25A: Test method for detection of alkali-silica reactive aggregate by accelerated expansion of mortar bars	Permits detection, within 16 days, of the potential for deleterious ASR of aggregate in mortar bars. Bars are soaked in 1N NaOH for 14 days. Because of severity this test should not be used alone to reject a given aggregate, nor should it be used to evaluate combinations of aggregates with cementitious materials.	ASTM C 1260: After 16 days, Exp < 0.10% indicates innocuous behavior. Exp > 0.20% indicates potentially deleterious expansion. Exp. between 0.10% and 0.20% may indicate deleterious or innocuous behavior, supplementary information required
	CSA-A23.2-27A: Standard practice to identify degree of alkali-reactivity of aggregates and to identify measures to avoid deleterious expansion in concrete (expansion limits)		CSA-A23.2-27A: After 16 days, Exp>0.150% potential reactivity. Exp>0.100% potential reactivity of quarried siliceous limestones from St. Lawrence Lowlands

Continued

<p><i>ASTM C 1567-08:</i> Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)</p>	<p><i>CSA A23.2-28A:</i> Standard practice for laboratory testing to demonstrate the effectiveness of supplementary cementing materials and lithium-based admixtures to prevent alkali-silica reaction in concrete</p> <p><i>CSA-A23.2-27A:</i> Standard practice to identify degree of alkali-reactivity of aggregates and to identify measures to avoid deleterious expansion in concrete (expansion limits)</p>	<p>Prisms cast and stored according to standard accelerated mortar bar test (ASTM or CSA). Used to test effectiveness of SCMs and. Test duration is retained at 16 days.</p>	<p><i>ASTM C 1567-07:</i> After 16 days, Exp < 0.10% indicate combinations of SCMs that will mitigate ASR effectively Exp > 0.10% indicate combinations of SCMs that may produce deleterious expansion in concrete, supplementary testing in ASTM C 1293 should be performed</p> <p><i>CSA-A23.2-27A:</i> After 16 days, Exp < 0.150% indicate combinations of SCMs that will mitigate ASR effectively</p> <p>Exp > 0.150% indicate combinations of SCMs that may produce deleterious expansion in concrete</p>
Concrete Tests			
ASTM Test Method	CSA Companion	Description	Expansion Limits
<p><i>ASTM C 1293-08b:</i> Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction</p>	<p><i>CSA A23.2-14A:</i> Potential expansivity of aggregates (procedure for length change due to alkali-aggregate reaction in concrete prisms at 38 °C)</p> <p><i>CSA-A23.2-27A:</i> Standard practice to identify degree of alkali-reactivity of aggregates and to identify measures to avoid deleterious expansion in concrete (expansion limits)</p>	<p>Commonly referred to as the concrete prism test, this test uses high-alkali cement with boosted alkalis (1.25% Na₂O_{eq}) and is conducted at nearly 100% humidity and 38 °C. Test is widely recognized as the best indicator aggregate reactivity compared to field performance. Test duration is 1 year.</p>	<p><i>ASTM C 1293-08b:</i> Exp ≥ 0.04% at 1 year indicates potentially deleterious expansion</p> <p><i>CSA A23.2-17A:</i> Exp > 0.040% at 1 year indicates potentially deleterious expansion</p>

Continued

<p><i>ASTM C 1293-08b:</i> Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction</p> <p>See Appendix for update, also in ASTM C 33-08</p>	<p><i>CSA A23.2-28A:</i> Standard practice for laboratory testing to demonstrate the effectiveness of supplementary cementing materials and lithium-based admixtures to prevent alkali-silica reaction in concrete</p> <p><i>CSA-A23.2-27A:</i> Standard practice to identify degree of alkali-reactivity of aggregates and to identify measures to avoid deleterious expansion in concrete (expansion limits)</p>	<p>Prisms cast and stored according to standard concrete prism test (ASTM or CSA). Used to test effectiveness of SCMs and lithium compounds. Test is then run for 2 years.</p>	<p><i>ASTM C 1293-08b:</i> Exp < 0.04% at 2 years indicates effectiveness of SCMs and/or lithium nitrate to control deleterious reaction due to ASR</p> <p><i>CSA A23.2-27A:</i> Exp < 0.040% at 2 year indicates effectiveness of SCMs and/or lithium nitrate to control deleterious reaction due to ASR</p>
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1.1.3.1 *ASTM C 1260 – Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)*

Often referred to as the accelerated mortar bar test (AMBT),³⁷ ASTM C 1260 was developed by the National Building Research Institute (NBRI) in South Africa as a method to rapidly identify potentially alkali-silica reactive aggregates by casting mortar prisms that measure 1 in. x 1 in. x 11.25 in (25 mm x 25 mm x 285 mm). An effective gage length of 10.00 ± 0.10 in. (250 ± 2.5 mm) is created by casting a stainless steel gage stud into each end of the mortar bars. For the initial 24 ± 2 hours, the bars are cured in a 100% relative humidity room at 73.4 ± 3 °F (23 ± 1.7 °C). The bars are then removed from the molds, measured and submerged in tap water. From this point on and for the remainder of the test, the bars are placed in an oven at 176 ± 3.6 °F (80.0 ± 2.0 °C). The initial or zero reading of the bars is taken 24 ± 2 h from placement in the tap water when the bars are also quickly transferred to a solution of 1N NaOH that has already been prepared and brought to 176 ± 3.6 °F (80.0 ± 2.0 °C). The mortar bars remain in the 1N NaOH soak solution for the next 14 days except when length

measurements are taken during the 14 day time period during the ± 2 h time window that the zero reading was previously taken. Length change is logged to the nearest 0.0001 inch and results are presented to the nearest 0.01% for the average of a minimum of three mortar bar prisms.³⁸

There are three categories that describe the criteria for expansion for ASTM C 1260, which is based on the expansion that occurs 16 days after casting (14 days after placement in 1 N NaOH). Expansion that is less than 0.10% is commonly a sign of non-expansive, innocuous behavior. Expansion that is more than 0.20% indicates that the aggregate used is potentially expansive and deleterious. Expansions between 0.10 and 0.20% suggest that the aggregate may demonstrate either innocuous or deleterious performance in the field.³⁸ Described in the non-mandatory appendix of ASTM C 1260, the discussed expansion criterion is not generally used by many researchers or agencies. Instead, the agreed expansion amid many ASR researchers and engineers is a particular expansion limit of 0.10% after 14 days of being immersed in the 1N NaOH soak solution.³⁹ Thomas and Innis⁴⁰ have demonstrated that the minimum level of a particular SCM required to control expansion with a given aggregate should be less 0.10% after 14 days of immersion in 1N NaOH (after 16 days total). This limit will be used in this report for determination of pass/fail criteria for a mixture tested in ASTM C 1260. Results up to 28 days will be presented for informational purposes only.

It should be noted that it is specified that ASTM C 1260 is to only be used for the testing of mortar. If coarse aggregate reactivity is to be assessed, the aggregate must be crushed to meet the gradation standards of the test.^{38, 41} This may lead to inaccurate reactivity predictions due to the altered physical characteristics of the aggregate when using ASTM C 1260 to assess potential behavior for use in a structure.^{4, 40}

1.1.3.2 *ASTM C 1567 – Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)*

ASTM C 1567 (AMBT) is a modification of ASTM C 1260 that replaces a specific percentage of cement with SCM material. The standard recommends testing the same aggregate and hydraulic cement without pozzolans or slag using Test Method C 1260. SCMs may be tested together or individually in binary or ternary blends to reveal a combination required to reduce expansion to a specified value (also generally 0.10% at 14 days). A high range water reducer (HRWR) may be used if necessary when testing blends containing silica fume or metakaolin and the water-cementitious ratio must remain at 0.47 by mass.⁴²

1.1.4 Specifications

1.1.4.1 *FHWA/AASHTO Guidelines*

Thomas et al. (2008) have recently developed guidelines for evaluating aggregate reactivity and selecting preventive measures to prevent or minimize ASR-induced expansion.⁴³ This approach, which was based largely on the CSA approach, provides both prescriptive guidance (e.g., alkali loadings of concrete, minimum SCM dosages, etc.) and performance-based guidance (based on ASTM C 1260 or ASTM C 1293). This approach is currently being considered by both ASTM and AASHTO in the form of recommended practices, standards, or specifications.

1.1.4.2 *Unified Facilities Guide Specification*

The Unified Facilities Guide Specification section 32 13 11 outlines the requirements for concrete construction projects performed by the United States Army, Navy and Air

Force for airfields, heavy-duty roads and hardstands, and vehicular pavement that exceeds 8000 cubic meters.⁴⁴ The document is inclusive of standards to be abided (ACI, AASHTO, ASTM, IPRF, NRMCA, CDT), specifications of proper construction equipment and material requirements, construction procedures, requirements of sampling and testing methods and reports, quality control techniques, repair and replacement procedures, as well as finished product specifications.⁴⁴ The procedures of this project will adhere to the requirements described by the Unified Facilities Guide Specifications to ensure consistency with ongoing concrete guidelines.

1.2 HYDRATION OF CEMENT AND SUPPLEMENTARY CEMENTITIOUS MATERIALS

1.2.1 Cement Hydration

Cement chemist notation is used to simplify formulas and is a "short hand" way of writing the chemical formulas that are composed of oxides of calcium, silicon, and various metals. The main oxides present in cement are abbreviated in the following way:

Table 1-2. Cement chemistry notation.

	Actual Formula	Name
C	CaO	Calcium oxide, or lime
S	SiO ₂	Silicon dioxide, or silica
A	Al ₂ O ₃	Aluminium oxide, or alumina
F	Fe ₂ O ₃	Iron oxide
T	TiO ₂	Titanium dioxide
M	MgO	Magnesium oxide
K	K ₂ O	Potassium oxide
N	Na ₂ O	Sodium oxide
H	H ₂ O	Water
\bar{C}	CO ₂	Carbon dioxide
\bar{S}	SO ₃	Sulfur trioxide
\bar{P}	P ₂ O ₅	Phosphorus hemi-pentoxide

The four main phases present in ordinary portland cement, known as the main crystalline phases of Portland cement, are presented in Table 1-3:

Table 1-3. Crystalline phases of anhydrous ordinary portland cement.

Notation	Actual Formula	Name	Mineral Phase
C ₃ S	3 CaO • SiO ₂	Tricalcium silicate	Alite
C ₂ S	2 CaO • SiO ₂	Dicalcium silicate	Belite
C ₃ A	3 CaO • Al ₂ O ₃	Tricalcium aluminate	Aluminate or Celite
C ₄ AF	4 CaO • Al ₂ O ₃ • Fe ₂ O ₃	Tetracalcium alumino ferrite	Ferrite

A discussion of the hydration of the individual portland cement components may provide a better understanding of the complex reactions taking place during cement hydration. Two mechanisms have been proposed to explain the hydration of portland cement. The first mechanism is known as the through-solution hydration and implies the dissolution of anhydrous compounds into their ionic constituents, hydrate formation in solution, and eventual hydrate precipitation from the supersaturated solution. A second mechanism, referred to as topochemical or solid-state hydration, occurs at the immediate surface of the anhydrous cement compounds without the compounds going into solution. From electron microscopic studies of hydration cement pastes, it has been proposed that the through-solution mechanism dominates during the early stages of cement hydration.¹⁹

There are four main phases present in the heterogeneous blend of ordinary portland cement: tricalcium silicate (C₃S), beta-dicalcium silicate (βC₂S), tricalcium aluminate (C₃A) and calcium aluminoferrite (C₄AF). The hydration rate of the compounds is not identical. The aluminate phases are known to hydrate faster than the silicates. As a

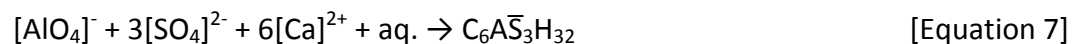
matter of fact, the hydration reactions involving the aluminates are largely responsible for the stiffening and setting of portland cement pastes.¹⁹

The hydration of the silicate phases, which make up approximately 75% of ordinary portland cement, affect the rate of strength development.¹⁹ The hydration reactions of aluminates and silicates will be discussed individually in order to develop an understanding of the chemical and physical transformations that occur during portland cement hydration.

1.2.1.1 Hydration of Aluminates

The reactions of C₃A and C₄AF take place immediately with the addition of water forming crystalline hydrates, such as C₃AH₆, C₄AH₁₉, and C₂AH₈. The presence of gypsum, which is approximately 5-6% in ordinary portland cement, slows the rapid hydration of C₃A, which would otherwise deem the portland cement unusable for most construction purposes. It is believed that the quick dissolution of gypsum and alkalis depresses the solubility of C₃A due to the presence of hydroxyl, alkali, and sulfate ions. In solutions saturated with calcium and hydroxyl ions, the crystallization of calcium aluminate trisulfate hydrate occurs as short prismatic needles and is often referred to as ettringite.^{19, 45, 46}

Ettringite:



Typically, ettringite is the first crystalline structure to form due to the high sulfate/aluminate ratio present during the first hour of hydration. Ettringite precipitation supports stiffening, setting, and early strength development. As sulfate is

depleted and the concentration of aluminate ions in solution rises again, ettringite becomes unstable and is converted into a monosulfate phase.



For so-called normal-setting portland cement, after about 45 minutes the rates of availability of aluminate ions and sulfate ions will be greatly reduced resulting in stiffening as ettringite crystals will fill spaces previously occupied by water.¹⁹

1.2.1.2 Hydration of Silicates

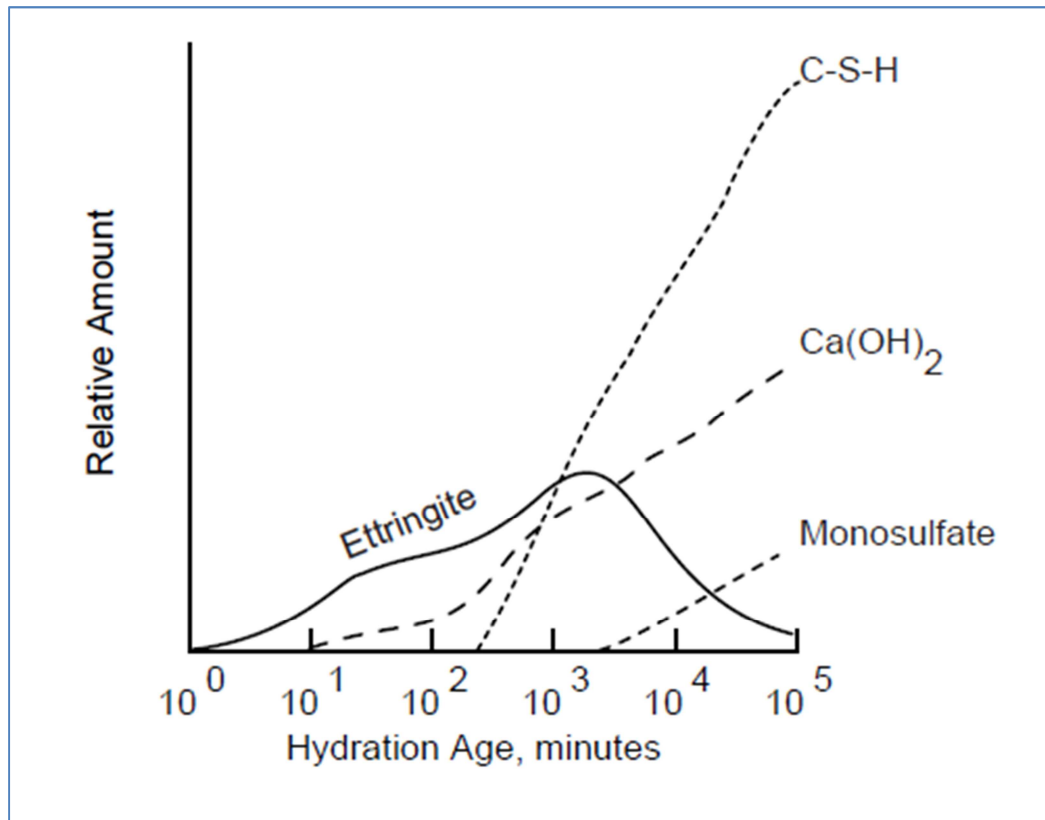
The hydration of C_3S and βC_2S produces a variety of calcium silicate hydrates as well as calcium hydroxide. The C-S-H structures, a chemical notation not implying a fixed chemical composition, are comparable but vary in calcium/silica ratio and bound water content. The compositional dissimilarities have little effect on physical characteristics. The material displays properties of a rigid gel as it is a porous solid with poor crystallinity and is often referred to as tobermorite, a naturally occurring mineral of similar structure. The composition typically used for stoichiometric calculations is $C_3S_2H_3$. As a result, the stoichiometric reactions for the hydration of C_3S and C_2S may be stated as follows:¹⁹



The hydration of the C_3S and C_2S is associated with the formation of calcium hydroxide where crystalline calcium hydroxide, portlandite, starts to form at the end of the induction period.^{7, 45} Portlandite is the second most abundant product in hydrated portland cement pastes. Due to its ability to be easily leached it is also the leading

contributor of hydroxyl ions (OH^-) to the liquid phase resulting in an increase in pore solution pH. Figure 1-1 displays the previously discussed formation rates for the hydration products of ordinary portland cement.

Figure 1-1. Typical rates of formation of hydration products in ordinary portland cement paste.¹⁹

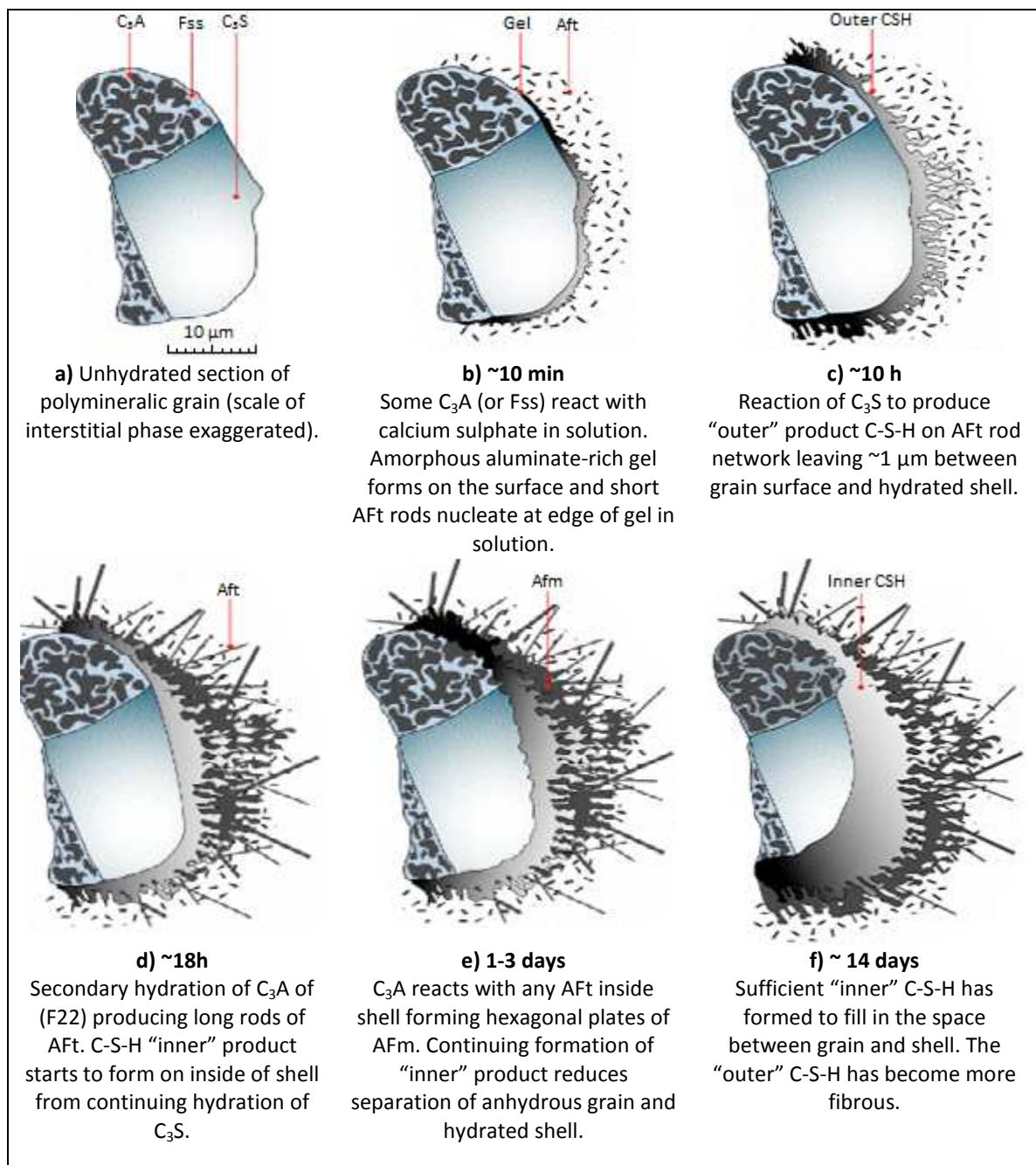


1.2.2 Kinetics of the hydration process

Calcium silicate hydrate (C-S-H) is the most prevalent component of hydrated portland cement paste and is a result of the hydration of the calcium silicates (C_2S and C_3S) phase hydration.⁴⁷ Following a rapid initial formation of small amounts accompanying the

hydration of C_3S in the pre-induction period, the amount of C-S-H is slowly increased in the induction period. This reaction rate of C-S-H formation is accelerated in the acceleratory stage and then gradually slowed again in the post-acceleratory stage, but may continue for months.⁷ Figure 1-2 displays the development of microstructure during the hydration of portland cement.

Figure 1-2. Development of microstructure during ordinary portland cement hydration.^{47, 48}



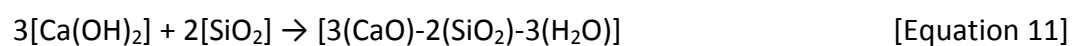
The C-S-H nanoparticles account for the long-term setting of cement paste through electrostatic forces.⁴⁹⁻⁵¹ However, it does not consistently possess long-range order and the intricate nature of portland cement hydration make it difficult to study. As a result, less complex methods of analysis including the study of the hydration kinetics of C₃S or the phase development of solution-derived C-S-H have been recently utilized and many studies have focused on pure C-S-H from the thermodynamic and structural perspective.⁵² Additionally, C-S-H may include limited amounts of Mg²⁺, Al³⁺, K⁺, Na⁺ or SO₄²⁻ in its structure.⁷

1.2.3 Pozzolanic reaction

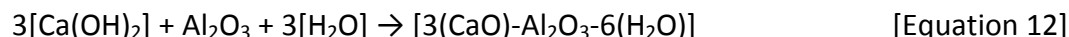
Natural pozzolans, when dispersed in saturated or almost saturated lime water, form C-S-H and hexagonal aluminates, C₄AH₁₃.⁷ At temperatures between 50 and 90°C, amorphous C-S-H is the main product of the pozzolanic reaction, as well as poorly crystallized tobermorite.⁷ This is similar to that obtained by the hydration of portland cement.⁵³ High-lime, i.e. high calcium, fly ashes may contain free lime which, upon mixing, are transformed into Ca(OH)₂ allowing hydration without the consumption of additional lime.⁷

The supplementation of pozzolanic materials in a blend containing portland cement can lead to the consumption of calcium hydroxide. An assumption may be made that the reaction of pozzolan and lime produces similar hydration products as cement by the following pozzolanic reactions:

Silicate:



Aluminates:



Due to the consumption of calcium hydroxide produced by portland cement hydration, the formation of supplementary hydrates can ultimately lead to a more durable product. This improved durability may be due, but is not limited to, the formation of a denser microstructure by C-S-H development, further binding of Na^+ and K^+ ions from solution, and/or the reduced concentration of hydroxyl ions in the liquid phase.⁷

1.3 MITIGATING ALKALI-SILICA REACTION

Common strategies for mitigating ASR in new concrete include limiting the alkali content of the cement, using nonreactive aggregates (rarely economically feasible), incorporating SCMs (fly ash, ground granulated blast furnace slag, silica fume, metakaolin, rice husk ash, and other natural pozzolans), and/or the use of chemical admixtures, namely lithium compounds.

1.3.1 Non-reactive aggregates

The utilization of nonreactive aggregates is undoubtedly the most effective method of preventing ASR because the reaction cannot take place without reactive silica. However, nonreactive aggregates are not readily available in many areas of the United States and may not be economically practical. Additionally, to define an aggregate as non-reactive involves stringent laboratory testing and satisfactory field performance records.

Standard tests of reactivity that have been previously described include ASTM C 1260 and ASTM C 1293. An aggregate may be used without additional precautions when considering its susceptibility to ASR if all of these conditions are met. If reactivity is detected, it may be recommended to integrate the use of suitable SCM(s) and/or

chemical admixture to the concrete, commensurate with appropriate testing to verify the efficacy of the chosen mitigation measure.

1.3.2 Supplementary Cementitious Materials (SCMs)

SCMs are mineral admixtures that are added to or replace a percentage of ordinary portland cement in order to complement the properties of hardened concrete through pozzolanic and/or hydraulic activity. SCMs are typically integrated into concrete mixtures to improve workability, setting time, strength development, permeability, resistance to freeze/thaw damage, acid and sulfate attack resistance, reinforcement corrosion resistance, and hinder alkali-silica related expansion.⁵⁴ However, the misuse of SCMs (overfinishing, overvibration, lack of quality control, combinations of SCMs with certain cements, etc.) can worsen premature deterioration.

Currently, the use of SCMs is the most common ASR mitigation strategy. There are three main ways that SCMs have been postulated to reduce ASR expansion when used appropriately; this includes: (1) lowering the overall concentration of available alkalis in the pore solution (2) binding alkalis in certain hydration products from the pore solution causing them to be unavailable for ASR expansive gel production and (3) lowering the permeability, which results in a decrease in water infiltration and movement.⁵⁵

Commonly used SCMs satisfy ASTM C 618 include Class C or F fly ash, ultra-fine fly ash, ASTM C 989 ground-granulated blast-furnace slag (GGBFS), ASTM C 1240 silica fume, and other industrial byproducts or natural pozzolans such as rice husk ash, calcined clay, and metakaolin. The use of fly ash and metakaolin in binary and ternary blends will be in the focus of this report.

1.3.3 SCM Classifications

SCMs can be categorized as hydraulic, pozzolanic, or both. Materials with hydraulic properties chemically react with water to form hydrated compounds with cementing properties very similar or identical to the products of portland cement hydration.

Materials that function hydraulically include ground granulated blast furnace slag (GGBFS), Class C fly ash, natural cement or cement rock, and hydraulic hydrated lime.

SCMs that react pozzolanically are highly siliceous or alumino-siliceous, and react with the calcium hydroxide that is formed by the hydration of portland cement to form cementitious compounds, namely calcium silica hydrate or C-S-H. Pozzolan materials include Class F fly ash, silica fume, metakaolin, clay and shale. Interestingly, if a reactive aggregate (e.g. containing silica) is ground finely enough to a powder form with a particle size distribution less than 0.2 inches (5 mm) it transitions from behaving like a reactive aggregate to a pozzolan and can be beneficial in reducing the potential for ASR.^{56 57}

The use of SCMs is the most common ASR mitigation strategy in concrete construction and there are a number of issues that affect the ability of any SCM to control ASR.¹⁶

These include inappropriate chemical/mineralogical composition, replacement dosage, aggregate reactivity, environmental exposure and the alkali content of the cementitious materials.¹⁶ Additionally, the mechanism(s) by which SCMs control expansion due to ASR vary considerably by material. These mechanisms include, but are not limited to, dilution of alkalis, entrapment of alkalis, microstructure alteration, and porosity and permeability reduction of the hardened concrete.

1.3.4 ASR Mitigation by Ternary Blends

The use of ternary blends, where portions of ordinary portland cement has been replaced by two separate SCM materials, has been shown to result in a significant reduction in ASR-induced expansion.⁵⁸ This is due to the formation of supplementary C-S-H^{59, 60} and in the case of metakaolin, calcium aluminate and calcium aluminosilicate hydrates through reaction with calcium hydroxide produced during portland cement hydration.^{59, 61, 62} Together, fly ash and metakaolin should result in densification of the concrete matrix and greater consumption of calcium hydroxide, yielding lower permeability^{63, 64} and decreased availability of calcium containing reactants (e.g., solid CH, Ca²⁺ in pore solution) in metakaolin binary blends.^{65, 66} The primary objective of implementing the use of ternary blends would be to incorporate fly ashes that were previously deemed unfit for ASR mitigation. Through coupling with metakaolin, fly ashes that pass ASTM C618 and C311 but exhibited poor performance in ASTM C1260 and were consequently formerly land-filled can now be used in concrete mixtures to combat ASR-induced expansion. It is believed that an increase in the alumina content of the overall blend due to the integration of metakaolin assist the fly ash in producing hydrates that obtain alkali binding characteristics. As a result, ternary blends containing fly ash and metakaolin can be a viable option In areas that have access to fly ashes that were previously considered unfit for ASR expansion mitigation.

1.3.5 Fly Ash

Fly ash is a by-product of the coal burning industry and is one of the most commonly used supplementary cementing materials. As one of the residues generated in combustion, fly ash comprises the fine particles that rise with the flue gases and is collected as an off-gas with bag filters or electrostatic precipitators before the flue gases reach the chimneys of coal-fired power plants. Dependent on the source of the coal, fly

ash is composed of various compositions of uncombusted mineral impurities from the coal that fuse together and solidify as they are transported from the combustion chamber and cooled. However, all fly ash includes considerable amounts of silicon dioxide (SiO_2) and calcium oxide (CaO).

Fly ash is classified by its chemical composition (based on CaO in CSA standards and the sum of $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2$ in ASTM standards). Additionally, the particle size distribution, morphology, and surface characteristics affect the water demand and workability of the fresh concrete material as well as the rate of strength development of hardened concrete.

The morphological properties, affected by the burning process for power generation, and the chemical composition of fly ash have a direct effect on the ash's ability to control ASR.⁷ This section will concentrate on how fly ash actually works to control ASR in concrete. ASTM C618 provides the specification for coal fly ash and raw or calcined natural pozzolan for use in concrete.⁶⁷ ASTM C311 covers the testing methods for sampling and testing fly ash and raw or calcined pozzolans for use in portland-cement concrete.⁶⁸ However, many fly ashes are rejected from use as a supplementary material due to reliability issues of the testing methods, particularly in determining the 'true' alkali contribution from fly ash. Despite these conflicts fly ash has become the most widely used SCM for use in portland-cement concrete due to the benefits resulting from its use, which may include:

- improved workability
- decreased water demand
- reduced heat of hydration

- increased ultimate strength
- reduced permeability
- improved durability
- reduced efflorescence
- decreased shrinkage
- improved resistance to ASR, sulfate attack, and corrosion

Class F fly ashes, having primarily pozzolanic properties, contain more than 70% silicon dioxide (SiO_2) plus aluminum oxide (Al_2O_3) plus iron oxide (Fe_2O_3) and are generally produced from the combustion of anthracite and bituminous coals.^{16, 67, 69} Class F fly ash lacks immediate strength qualities, but through pozzolanic action can significantly enhance the long-term strength of concrete.^{54, 70}

Class C fly ashes contain greater than 70% silicon dioxide (SiO_2) plus aluminum oxide (Al_2O_3) plus iron oxide (Fe_2O_3) and are products of lignite and sub-bituminous coal combustion.⁶⁷ Class C ashes are more reactive due to being made up of reactive crystalline compounds and typically possess better early strength qualities. Class C ashes possess both hydraulic cementing as well as pozzolanic properties.⁵⁴ Class C fly ashes often possess enough CaO (lime) to be self-cementing, which when coupled with pozzolanic action can result in faster early strength gain than Class F fly ashes.⁷¹

Fly ash is predominantly silicate glass containing silica, iron, calcium, alumina and minor amounts of potassium, carbon, sodium, sulfur and magnesium. Fly ash has a spherical shape that generally ranges in size from $<1\ \mu\text{m}$ to $100\ \mu\text{m}$ in diameter, the majority being less than $20\ \mu\text{m}$ in size and present as solid spheres, though many particles are

present as cenospheres.²⁰ The resulting product, composed primarily of solid spheres, appears as a finely divided powder resembling portland cement to the naked eye.⁵⁴

1.3.6 Metakaolin and other natural pozzolans

Natural pozzolans are primarily composed of aluminosilicates in a very disordered structure, which, in addition to having a high porosity and surface area, results in a highly reactive material. This amorphous structure is not stable in alkaline solutions, and thus bonds easily with lime or portland cement in an aqueous environment.

For calcined clays, the pozzolanic reactivity is associated with the removal of the structural water from the crystalline clay layers. The process results in a product that is amorphous or semi-amorphous and possesses a high surface area and high chemical reactivity.⁷² The first use of the pozzolanic metakaolin dates back to 1962 when it was used in concrete for the construction of the Jupia dam in Brazil. In contrast to fly ash, metakaolin is not the by-product of an industrial process and is produced by the calcination of kaolinitic clay. Metakaolin must be manufactured under a carefully controlled process involving thermal activation in a kiln (650-800°C) before being crushed to a fine particle size of 1-2 µm. After dehydration at roughly 100°C, kaolinite breaks down and releases its hydroxyl components in the form of water leaving behind a mixture primarily composed of alumina and silica.⁷³ Further calcination maximizes this primarily amorphous material's reactivity by producing an anhydrous alumino-silicate ($\text{Al}_2\text{Si}_2\text{O}_7$) that performs as a highly reactive artificial pozzolan.^{74, 75} Produced by the dehydroxylation of phase pure kaolin, the base structure of metakaolin is a highly disrupted phyllosilicate structure comprising silica and alumina; though a large amount of commercially produced metakaolin includes minor levels of impurities, predominantly muscovite and titanium oxide.⁷⁶

Conforming to ASTM C 618, metakaolin is considered highly reactive and is typically composed of 50-55% silicon dioxide (SiO_2) and 40-45% aluminum oxide (Al_2O_3).⁶⁴ When metakaolin replaces cement by 5-15%, an increase in compressive strength may exist for high-performance concretes and mortars, particularly at early ages.^{74, 77} There are three factors that affect how metakaolin contributes to strength when used to partially replace cement in concrete. These include the filler effect (i.e. particle packing and densification), acceleration of portland cement hydration, and the pozzolanic reaction with calcium hydroxide.⁷⁷ Sabir et al. showed that particle size and decreased specific surface has a direct relation on prolonging the duration at which metakaolin contributes to elevated concrete strengths. An increase in fineness was also found to increase the optimum level of replacement of cement without any damaging affects due to dilution.⁷³

The hydration of portland cement alone typically results in 20-30% of the resulting paste mass to be composed of calcium hydroxide. When used as a partial replacement for portland cement, metakaolin reacts with portlandite to create supplementary C-S-H that is comparable in constitution to C-S-H from portland cement alone, thus reducing overall amounts of calcium hydroxide.⁷⁵ Furthermore, blends containing metakaolin have improved permeability and as a result, metakaolin has earned recognition as an effective material for the suppression of alkali silica reaction expansion.^{74, 77}

The particle size of metakaolin is considerably smaller than other SCMs varying to some degree, but typically less than 5 μm , with the average size of being roughly 1.5 to 2.5 μm .^{78, 79} Based on MAS-NMR, metakaolin is composed of alternating layers of buckled silicate in 4-coordination and alumina in a combination of 4-, 5-, and 6-coordination.⁷⁶ From X-ray analysis the structure of metakaolin appears disordered, but Lee et al.⁸⁰

observed with Energy-Filtering Transmission Electron Microscopy (EF-TEM) that since metakaolin is derived from the dehydration of hydroxyl groups from the layered kaolinite structure then some degree of order must exist. Since then, it has become accepted that metakaolin reactivity is dependent on the strain in the bonding network generated by thermal dehydroxylation⁸¹ that causes a change in the coordination number of the contained alumina from primarily a 6- to a mixture of 4-, 5-, and 6- coordination.⁸²

1.3.7 Mechanism by which Fly Ash Controls ASR

For alkali-silica reaction mitigation efforts fly ash is the most used SCM, the efficiency of which depends on several parameters that include:¹⁶

- Dosage of fly ash (typically mass replacement by percentage of cement)
- Chemical composition (particularly the lime (CaO) content and alkali content)
- Aggregate reactivity
- Chemical composition of the concrete (particularly the cement alkali content).

Although it is not yet completely understood how fly ash provides ASR mitigation, research over the past 20 years has elucidated several ways in which fly ash reduces this reaction. The development of supplementary C-S-H through pozzolanic reaction of fly ash with portland cement hydrates (and subsequent depletion of CH) leads to a denser microstructure and a reduction in capillaries that allow the movement of moisture through the concrete. The resulting matrix has a lowered permeability and thus a reduced ease of access for water to saturate and form alkali silica gel.⁷¹ The supplementary C-S-H formed from the inclusion of fly ash (in particular lower lime ashes) has been found to be capable of binding alkalis long-term. The entrapment of

alkalis in cement hydrates renders them unavailable for participation in deleterious alkali-silica reactions.^{75, 83}

There are three characteristics that attribute to the effectiveness by which fly ash can mitigate ASR expansion: fineness, mineralogy, and chemistry. The use of finer pozzolans creates a denser material that reduces the permeability of the matrix and penetration of water into the system. An optimum mineralogy of the fly ash will provide chemical components that are properly bound and/or able to chemically react with the other constituents. Lastly, in order to provide the best balance of constituents to mitigate expansion, the chemical components of the fly ash are also of importance.

High-calcium fly ashes (Class C) contain 30-50% calcium-oxide and some have been seen to possess an affluence of readily available alkalis.⁸⁴ Class C fly ashes tend to require higher dosages for ASR mitigation than their counter-part (Class F fly ash) discussed below; an aspect that is not generally preferred.¹¹ Additionally, the C-S-H structure produced by the incorporation of Class C fly ash is likely to have a higher C/S ratio that supports either a neutral or positive excess charge that has very little likeliness for absorbing alkalis.⁷

Low-calcium fly ashes (Class F) have increased silica and alumina concentrations compared to Class C fly ashes, and are generally more effective in controlling ASR expansion. It is believed that this is a result of a decreased calcium to silica atomic ratio (Ca/Si) in the C-S-H structure of the hardened concrete.¹⁹ This lower Ca/Si ratio produces a negative surface charge within the C-S-H structure developing the ability of the hydration products to bind the positively charged alkalis.^{11, 85, 86} Additionally, alkalis contained by Class F fly ashes are not as readily available as those contained by portland

cement. As a result, a dilution effect occurs where the overall concentration of available alkalis that could contribute to ASR expansion is reduced.^{16, 87} However, this remains a topic of debate and further research.

1.3.8 Mechanism by which Metakaolin and other Natural Pozzolans Control ASR

Natural pozzolans mitigate expansion due to alkali-silica reaction through alkali entrapment and ion exchange. Containing between 5% and 10% calcium, the supplementary C-S-H formed from the incorporation of metakaolin has a low Ca/Si ratio (in the range of 0.8 to 1.5), which promotes the entrapment or binding of alkali ions from the pore solution.⁸⁸ Used in dosages around 10% of the cement mass, the use of metakaolin results in a reduction of alkalinity (and associated pH) in the pore solution and a depletion of portlandite; two aspects that are considered to be the most effective of pozzolans in reducing ASR expansion.^{17, 88-90}

Malquori⁹¹ and Turrizani⁹², and more recently DeSilva⁹³ et al., have discussed the chemical reactions involved when calcined clays are used as pozzolans for concrete. The reaction occurs principally between the alumino-silicate products (AS) of the metakaolin and the calcium hydroxide (CH) derived from cement hydration, in the presence of water. Additional cementitious C-S-H containing aluminum is formed, C-A-S-H, as well as other crystalline products that include calcium aluminate and alumino-silicate hydrates (i.e., C_2ASH_8 , C_4AH_{13} and C_3AH_6); the production of which depends on the AS/CH ratio and reaction temperature^{73, 94, 95}. Metakaolin also influences the microstructure and diffusion properties of blended cement pastes and concrete.^{73, 88, 96, 97} Blended pastes containing metakaolin possess a finer pore structure compared to plain cement pastes⁹⁶ as well as a reduced rate of diffusion of Na^+ ions and rate of water absorption.^{73, 88}

1.3.9 Material Properties of fly ash and metakaolin

The use of SCMs varies by application and dosage depending on the desired effect and its physical makeup. Physical characteristics of portland cement, Class F and C fly ash, and metakaolin are provided in Table 1-4. Typical replacement dosages for ASR control are also included.

Table 1-4. Physical properties of ordinary portland cement, fly ash, and metakaolin.

	Specific gravity	Surface area (m ² /kg)	Bulk Density (kg/m ³)	Particle diameter (μm)	Typical replacement (% by mass)	Color
Portland Cement	3.15	350	830-1650	10.0-15.0	/	Tan
Fly Ash - Class C	1.9-2.8	300-500	540-860	1-100 avg: <20	15-50	Tan
Fly Ash - Class F	1.9-2.8	300-500	540-860	1-100 avg: <20	15-30	Brown
Metakaolin	2.40-2.61	650-1350	300-400	1.0-2.0	5-35	White

Sources: ^{54, 98-102}

Effect due to the use of individual SCMs on select concrete properties is presented in Table 1-5. Evaluation of the effects due to specific SCM use may lead to the consideration of ternary blends, using two SCMs coupled with ordinary portland cement to create a concrete with particular qualities. A plus indicates improvement in the property, a minus indicates a reduction.

Table 1-5: SCM Reactivity and Effects on Fresh and Hardened Properties

	Workability	Early-Age Strength	Long-term Strength	ASR Mitigation
Class C Fly ash	++	+++	++	+
Class F Fly ash	++	-	++	+++
Metakaolin	-	+	++	+++

The physical characteristics of fly ash, being small and spherically-shaped, gives rise to particle packing and a corresponding denser paste matrix. An eventual disappearance of the interfacial transition zone, by reason of particle packing and pozzolanic reaction, can give rise to a highly durable and crack-resistant product.¹⁰³

1.3.10 Major Constituents of Fly Ash and Metakaolin

1.3.10.1 Alkalies (Na_2O and K_2O)

The efficacy of SCMs to control expansion due to ASR is interrelated to their ability to lower the alkalinity and concentration of hydroxyl ions (OH^-) in the pore solution.^{75, 84}

The use of fly ash and metakaolin both amplify the ability for the hydration products to bind alkalis, thus reducing their availability in the pore solution by increasing the silica and alumina content. As the calcium content decreases, the surface charge of the hydration products (namely C-S-H) becomes more negative. As the hydration products are populated with more negatively charged sites increasing amounts of alkali cations (Na^+ and K^+) are attracted.⁷⁵ Recent research has shown that in blends made with portland cement and a SCM the alkalis from the portland cement are released more readily than the alkalis from an SCM. This is dependent on the reactivity of the particular SCM and the source of alkalis within the SCM. Alkalies released into the concrete matrix either become bound in the solid hydrated phase, released to the liquid pore solution, or they remain bound in non-reactive crystalline phases.⁷

The alkalis in the pore solution are directly correlated to the alkali, calcium, silica, and alumina content of the cementing materials. A mathematical relationship has been derived by Thomas et al. to determine the OH^- or ($\text{Na}^+ + \text{K}^+$) concentration of the pore

solution depending on the chemical composition of the cementitious blend. This relationships are expressed in Equations 13 and 14 below:¹⁰⁴

$$\text{OH}^- = 6 \times (\text{Na}_2\text{O}_e * \text{CaO}) / (\text{SiO}_2)^{16} \quad [\text{Equation 13}]$$

Where,

$$\text{Na}_2\text{O}_{\text{eq}} = \text{Na}_2\text{O} + 0.658 \times \text{K}_2\text{O} \quad [\text{Equation 14}]$$

$\text{Na}_2\text{O}_{\text{eq}}$ = total sodium oxide equivalent, in percent by mass

Na_2O =sodium oxide content, in percent

K_2O =potassium oxide content, in percent

The total available alkalis ($\text{Na}^+ + \text{K}^+$) are represented by Na_2O_e , as presented by Equation 14¹⁶, which signifies the quantity of alkalis in the portland cement. The calcium to silica ratio, on the other hand, is a representation of the binding capacity of the hydrates. As the alkali concentration of the pore solution drops, alkalis from the hydrates are released to maintain equilibrium between the solid and liquid phases.⁸⁵ Both CaO and SiO_2 affect the amount of calcium and silica ions in the system thus affecting the amount and/or composition of the hydrates. As the amount of silica increases, the Ca/Si ratio of the hydrates decreases, resulting in a greater removal of alkalis from the pore solution and therefore a lower alkalinity of the pore solution.⁸⁴

When an alkali-silica reactive aggregate is introduced to the system, alkali-silica reaction may decrease the pH of the pore solution as a result of released silica combining with hydroxyl ions. As a result, the hydrates release alkalis to maintain equilibrium, which are then added to the released silica and hydroxyl ions to form the alkali-silica rich gel.⁸⁶

1.3.10.2 Calcium Oxide (CaO)

The CaO content of fly ash is typically considered as the most imperative parameter when assessing how well it may control ASR. This is due to the fact that as the amount of CaO within a fly ash increases the efficiency of such fly ash will decrease. This is typically due to the level of beneficial SiO₂ being reduced, which reduces the amount of calcium hydroxide that can be converted to C-S-H. As a result, in order to control a given reactive aggregate, higher replacement levels of fly ashes that are abundant in CaO will be necessary in comparison to fly ashes with low CaO contents. Low-calcium fly ashes also have a reduced amount of alkalis readily available for reaction compared to those contained in high-calcium ashes which tend to be more readily available to go into the pore solution.^{16, 105} As a result, Class F fly ashes generally require lower replacement dosages (15-25 %) compared to Class C fly ash dosage rates (25-40% and higher).¹⁶

Metakaolin contains very low levels of CaO (typically below 5%) as it is primarily composed of silicon dioxide and aluminum trioxides. As a result, generally, lower amounts of metakaolin are required to lower the overall CaO content of a concrete mixture and introduce SiO₂ and Al₂O₃ for supplementary C-S-H development.

1.3.10.3 Silicon dioxide (SiO₂)

Low calcium Class F fly ashes contain a higher silica concentration than Class C ashes, leading to production of a C-S-H structure with a lower calcium to silicon ratio.^{9, 106} Silicon dioxide also make up about 50 percent of metakaolin, which also results in a lower Ca/Si ratio in the supplementary C-S-H. With a decreased Ca/Si ratio this supplementary C-S-H has an increased affinity for binding alkalis from the pore solution.⁶

1.3.10.4 Aluminum trioxide (Al_2O_3)

It is believed that Al_2O_3 can contribute to the pozzolanic effect of silica and a relationship may exist between increasing the sum of $SiO_2 + Al_2O_3$ and deleterious ASR mitigation.^{64, 106} Thus, studies have concluded an inverse correlation between expansion and the total cementitious Al_2O_3 content.^{9, 64} When physically dispersed into C-S-H, it is believed that alumina reacts slowly to create a supplementary C-S-H created by the use of SCMs containing Al_2O_3 , often referred to as C-A-S-H, and may have further increased affinity to bind alkalis from the pore solution. It is assumed that alumina replaces silica at tetrahedral sites within the C-S-H creating a negative charge region capable of binding a positively charged alkali ion.^{5, 6} Additionally, the preference of fly ashes containing higher levels of Al_2O_3 may also contribute to the hindrance of silica dissolution from reactive aggregate. It is known that when alumina molecules are present in a high pH solution they are more easily fragmented than silica molecules. As a result, the dissolution of silica products into the ITZ or pore solution to contribute to charge balance would be lessened due to the presence of alumina products.³¹

1.4 FOCUS ON ALUMINA IN SCMS FOR CONTROLLING ASR

It has been shown in limited research that the addition of particular forms of alumina through the incorporation of SCMs such as fly ash and metakaolin can enhance the ability for such SCMs to improve durability issues by promoting alkali sorption into the solid hydrate phases with an associated reduction of pore solution alkalinity.^{5, 30} As a result, a fly ash containing elevated amounts of alumina could be preferred. Metakaolin, which has an even higher level of alumina, may be utilized in even lower quantities to control deleterious ASR when tested in standard laboratory tests.³¹

However, it should not be concluded that all fly ash with considerable amounts of alumina will suppress expansion. The consideration of alumina has not been entirely investigated by other test methods.

1.4.1 Alumina and C-A-S-H development

The introduction of alumina into C-S-H for the development of a C-A-S-H structure may enhance the alkali binding capacity of a hydrated concrete system. The effects from the introduction of acidic ions, particularly 4-coordination alumina, into the tetrahedral sites of a C-S-H gel introduces a mechanism for alkali substitution in which charge balance is maintained by a double substitution for silicon:⁵



where M⁺ is (Na, K). Alumina occupies tetrahedral sites directly replacing Si while the alkali ion occupies otherwise empty sites.⁵

It is known that for metakaolin, when immersed in an alkaline solution, an attack on the structure occurs that results in the release of silicate and aluminate species into solution. Upon dissolution, as evidenced by ²⁷Al and ²³Na MAS NMR techniques, 5- and 6-coordination alumina is converted to a primarily 4-coordination.¹⁰⁷ The formation of 4-coordination alumina may be essential for the binding of alkalis from solution during the formation of C-A-S-H. A similar mechanism may exist for alumina contained by fly ash depending on the form of alumina contributed. Additionally, the initial release of alumina is believed to be more rapid than that of silica.¹⁰⁸ It may be possible that the dissolved alumina can react with the dissolved silicate and alkaline solution to form aluminosilicate oligomers which grow to form a crystalline structure.¹⁰⁹ The resulting structure contains silica and alkalis, as does alkali-silica gel produced during the ASR

process, but the incorporation of alumina may result in a structure that does not exhibit the desire to imbibe water and expand.

The amount of available alumina as well as the rate of its release can affect strength and other properties of fresh and hardened concrete including setting traits, acid resistance, microstructure development, and strength change profile. Elevated temperatures hinder the crystallization of phases that include aluminate ions, while in contrast it enables the decomposition of an aluminosilicate structure and the formation of a C-S-H phase that supports the substitution of silica with alumina and the creation of tobermorite, the structural model for many C-S-H samples.⁷⁶ Tobermorite and jennite, often used as model compounds for C-S-H, are both layered minerals composed of Ca-O sheets ribbed with silicate chains that repeat every 3 tetrahedral units (i.e., dreierketten).¹¹⁰ Black et al. found that, considering tobermorite composition and the Lowenstein's rule that Al-O-Al linkages are forbidden, alumina substitution for silica is possible up to $\text{Al}/(\text{Si}+\text{Al})=1/6$ causing the chemical composition to vary from $\text{Ca}_{4.5}\text{Si}_6\text{O}_{16}(\text{OH})\cdot 5\text{H}_2\text{O}$ (natural tobermorite) to $\text{Ca}_{4.5}\text{AlSi}_5\text{O}_{15}(\text{OH})_2\cdot 5\text{H}_2\text{O}$ in a fully exchanged tobermorite.¹¹¹

Dissolved alumina is known to enter the calcium silicate hydrate phase (C-S-H) of portland cement where substitution for silica is foreseen to play a worthy function in cation and anion exchange behavior, solubility, and reaction progress during delayed ettringite formation (not discussed in further detail).³⁰ It is the mechanisms of this substitution and its influence on the behavior of cement systems that has become a subject of considerable discussion. Kalousek¹¹² revealed that alumina enters the tobermorite structure by substitution of silica primarily at tetrahedral sites, introduced early as 4-coordination, and other spectroscopic studies have helped assist in the

understanding of the role of alumina in C-S-H and its model compounds, tobermorite and jennite. Other studies have also been conducted to assist in the interpretation of the data for aluminous C-S-H on solutions containing alumina, aluminate cements, Al-free C-S-H, tobermorite, jennite, and other materials.³⁰

It has also been shown that both 4- and 6-coordination alumina arise in the C-S-H of ordinary cement systems¹¹³ and alumina can also occur in both ettringite and AFm of such systems.^{114, 115} A structural model has been suggested by Lognot et al.¹¹⁶ that incorporates 6-coordination alumina in the interlayer and 4-coordination alumina in both the bridging and pairing tetrahedral of the chains and proposed that sodium plays a key role in charge balancing silica substitution by alumina.¹¹⁷⁻¹²⁰ Since then, the presence of 4-, 5-, and 6-coordination alumina has been confirmed by Andersen et al.¹²¹⁻¹²³ in precipitated C-S-H and cement paste systems hydrated at various lengths of time. They also confirmed previous results that 4-coordination alumina occurs on only bridging tetrahedral of the drierkette aluminum-silicate chains; 5-coordination alumina occurs in the C-S-H interlayers; and 6-coordination alumina occurs in hydrous aluminate or calcium-aluminate phase associated with the C-S-H particle surfaces. However, it has been argued that, based on structural-chemical factors, 6-coordination alumina cannot occur on the calcium sites of the Ca-O sheet.³⁰

In C-S-H modeled by tobermorite, 4-coordination alumina must be charge balanced by a single charged cation due to the difference in charge between Al^{+3} and Si^{+4} . Alumina occurring in bridging tetrahedral sites may be charge balanced by alkalis contained in solution, Ca^{+2} , or H^+ (OH-groups).³⁰ Additionally, the 5-coordinationa and 6-coordination arrangements may also require charge balancing by Na^+ and Ca^+ , and Bunker et al.¹²⁴ illustrates possible nearest- and next-nearest-neighbor configurations.

It has been proposed that the superior effectiveness of metakaolin to mitigate ASR may be directly related to their elevated alumino-siliceous chemical composition.

Mechanisms such as the alteration in the alkali adsorption capacity of the paste fraction and alkali activation of pozzolanic SCMs may contribute to the reduction in expansion.⁵⁸

It is still unclear which solid phase or phases of the concrete matrix may be responsible for binding alkalis. In the past, suggestion has been given to calcium silicate hydrate (C-S-H), the most copious phase in paste. Additionally, an increase in alkali binding has been seen to be responsive to the reduction of the Ca/Si ratio of the gel. Research by Hong and Glasser suggested that alkalis can be bound into C-S-H at acidic silanol, Si-OH, sites. It has been further suggested that alkali binding can be intensified through the incorporation of tetrahedral Al into C-S-H which results in acidity at those sites. When physically dispersed into C-S-H, alumina reacts slowly to form C-A-S-H. With further dispersion into solid solution, the alkali sorption potential increases. This mechanism proposed by Hong and Glasser suggests that Al replaces Si at tetrahedral sites creating a negative charge region that that may be capable of binding a positively charged alkali ion.^{5, 6} As discussed in Section 2, any alkalis present disassociate in the pore solution leaving K^+ and Na^+ that must be charge balanced in order to create equilibrium by the transfer of hydroxyl ions from the concrete matrix resulting in the triggering of the ASR reaction.¹⁶ The removal of such alkalis from solution coupled with the reduction in pH and concentration of hydroxyl ions may delay or completely hinder the initiation of ASR.

1.4.2 Geopolymer development

A second mechanism that may be responsible for alkali sorption is borrowed from research related to alkali activated fly ash concrete (concrete without ordinary portland cement). The process involves geopolymerization development between a material rich in aluminosilicate oxides and an alkali solution under highly alkaline conditions.

Generally, an aluminosiliceous source (such as fly ash or metakaolin), an alkali metal hydroxide or alkali silicate source, and water are required for the synthesis of geopolymers.¹²⁵ According to Glukhovsky, breakdown of the covalent bonds in Si-O-Si occurs when the pH of the alkaline solution is raised. When alumina is present, geopolymerization results from condensation and cross-linking of –Si-O-Al-O– silicate links into a three dimensional network.¹²⁶ The structure type of this geopolymer framework would be made up of 4-coordination silica and alumina tetrahedral molecules. Similar to C-A-S-H, the incorporation of tetrahedral Al may result in an acidic location in the form of a geopolymer that would be charged balanced by the adsorption of alkali ions. Unlike the C-S-H phases, where structural details are based on crystal structure, details of geopolymer formation in the binder phase are particularly unidentified.¹²⁷ Additionally, it has become well known that geopolymers are heterogeneous, possibly implying that their formation in a concrete matrix would be irregular and sporadic. As a result, currently, the development of such geopolymers in actual concrete incorporating alumino-siliceous materials has not been fully investigated.

Paralleled to this possible geopolymer gel formation, the presence of calcium and the corresponding development of C-S-H and C-A-S-H results in water deficiency and a rise in alkalinity. The increased alkalinity accelerates the dissolution of silicate and aluminate species that in turn increases the rate of poly-condensation and geopolymerization. As a result, the presence of calcium contributes to the mechanical strength of the resulting hardened matrix not only by forming C-S-H and C-A-S-H but also by enhancing the geopolymerization process.¹²⁸ However, the geopolymerization and binding of alkalis is limited by the availability of alumina to form tetrahedral bonds and cross linking of –Si-O-Al-O– silicate links into a three dimensional network. This mechanism may be responsible for a lack of correlation between differing test methods

used to evaluate various highly reactive aggregates. The NaOH soak solution used in ASTM C1567 has the potential to act as an activator solution for the alumino-siliceous material to promote geopolymerization of –Si-O-Al-O sialate links and result in alkali binding mechanisms that do not exist in other test methods or in field applications. This is an area for future research.

1.4.3 Dissolution of silica

A final mechanism to possibly describe the role of alumina in ASR expansion mitigation is its ability to lower the rate of dissolution of silica into solution from the reactive siliceous materials present in the fine or coarse aggregates. The availability of dissolved alumina has been found to hinder silica dissolution by the sorption of dissolved alumina onto silica particles in geopolymer gel formation.¹²⁵ It is unclear if this would apply to alumina adsorbing to the surfaces of damaged siliceous reactive aggregate or to coagulated species of dissolved silica around the aggregate or in the pore solution. In either case, it is believed that the presence of alumina may play a role in slowing down or even blocking the rate of silica dissolution. A major factor in the ability of alumina to hinder the dissolution of silica is directly related to its rate of participation in the network. Whether this impacts the service life of a structure long term is another question since the driving forces of ASR may be capable of overcoming the initial suppressive nature of alumina on silica dissolution.

1.5 SUSTAINABILITY

Concrete is an environmentally sound building material as concrete roads and buildings last longer and require less maintenance than other building materials. When concrete is used as the material for freeways, less consumption of vehicle fuel can result. Recent studies have also determined that using lighter colored concrete products rather than

asphalt pavement can help to reduce excessive surface temperatures due to radiation, thus further conserving energy.¹²⁹ Concrete can be made more sustainable, however, with the use of supplementary cementitious materials. Replacing portions of portland cement with SCMs can assist in reducing the depletion of natural resources (otherwise used for portland cement production) and can significantly decrease the energy-intensive manufacturing of portland cement. Thus, savings in both energy usage as well as greenhouse gas emissions result from the use of SCMs in concrete. Supplementing fly ash in concrete also qualifies for credit under the U.S. Green Building Council's LEED rating system for sustainable development and construction.¹³⁰

As documented by industry providers, more than 12 million tons of coal fly ash are used in concrete products in America each year, while another 34 million tons of coal combustion products are used in other applications such as gypsum wallboard, stabilizing soils, structural fills, road base materials and agricultural uses.¹³⁰ The American Coal Ash Association (ACAA) estimates that a one-ton replacement of fly ash for portland cement in concrete can offset the carbon dioxide emission from the manufacture of portland cement by an equivalent one-ton. The space saved by not land filling this amount of material would allow for an additional 455 days of solid waste produced by the average American. This amounts to enough energy saved to power the average American's home for 24 days. Since 1966 the production of coal combustion products has increased by 450%. However, in that same time period there has only been an increase in use of that material from 18% in 1966 to just over 40% in 2007.¹³¹ Certainly there exists a great deal of material that is currently land filled that could be potentially reclaimed for use in wide variety of applications.

The supplementation of previously deemed unusable fly ash with the addition of metakaolin can further improve the effect of fly ash and reduce its impact on landfills. Although the production of calcined clays is energy intensive, its impact on the environment in terms of greenhouse gas emissions is greatly reduced when compared to the production of portland cement. Furthermore, the energy used for the production of such calcined clays would be offset by the use of fly ashes that would otherwise be discarded.

Supplementing portland cement with fly ash and/or metakaolin results in an increase in durability of the concrete in turn increasing the life of roads and structures. By increasing the durability the necessity for eventual reconstruction and maintenance decreases, resulting in a lower total embodied energy of the material.

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2 FIRST MANUSCRIPT: ALKALI-SILICA REACTIVITY AND THE ROLE OF ALUMINA

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Abstract: In this study, the effect of alumina from supplementary cementitious materials (SCMs) or by direct addition on potentially alkali-silica reactive aggregates was investigated using the accelerated mortar bar test (AMBT). The study was done using two types of ternary blends: high-alkali portland cement with fly ash and alumina powder, and high-alkali portland cement with fly ash and metakaolin. Results show that mixtures containing an overall higher level of alumina showed improved alkali-silica reaction (ASR) expansion mitigation capabilities when analyzed using AMBT. The results herein show the improved potential for blends containing an overall higher level of alumina to suppress expansion due to ASR.

2.1 INTRODUCTION

Alkali-silica reaction (ASR) is an internal chemical reaction in concrete that has resulted in premature deterioration of various concrete structures worldwide. The reaction is driven by a high pH concentration in the pore solution of the concrete (usually between 13.2 and 13.8). The presence of alkalis from Na_2O and K_2O produce an increased pH by disassociating in solution causing positively-charged Na^+ and K^+ to be balanced by negatively charged OH^- ions. The reaction is also dependent on the presence of reactive aggregate. An aggregate is generally considered reactive if mortar bar expansion containing the aggregate is greater than 0.10% at 14 days.¹ The increase in $[\text{OH}^-]$ initiates an attack on the reactive aggregate that causes the dissolution of silicate species. A coagulation of this silicate species with the alkali ions produces a gel-like material that absorbs water, resulting in expansion that puts the concrete in tension. Previous studies have stated that the variable chemistry of this alkali-silica gel (ASG) is characterized by the dominance of Si^{4+} , with minor amounts of Ca^{2+} , Na^+ , and/or K^+ .^{2, 3}

Production of cement not only consumes large amounts of energy, but could also account for approximately 10% of total anthropogenic CO_2 emissions in the close future⁴. The use of fly ash, a product of coal combustion that would otherwise be land filled, may be used as a supplementary cementitious material (SCM) to reduce energy demands and greenhouse gas emissions in addition to mitigating ASR damage. Fly ash is also preferred due to its added ability to improve workability as well as increase strength and long-term performance of hardened concrete. Particular fly ashes used at replacement levels of up to 40% have been found effective in significantly reducing expansion and cracking of hardened concrete.⁵ However, inconsistency in fly ash properties (due to combustion, collection processes, and differing sources of coal) and some unfavorable properties at higher replacement rates, such as delayed set times,

have limited its use as a replacement for portland cement at replacement levels higher than 30%.

Metakaolin is a material that may be suitable to complement fly ash for the purpose of ASR mitigation. Made up of primarily alumina and silica oxides, metakaolin is manufactured under a carefully controlled process by thermally activating purified kaolinite clay within a specific temperature range (650-800°C). The resulting anhydrous alumino-silicate ($\text{Al}_2\text{Si}_2\text{O}_7$) is mainly amorphous material that behaves as a highly reactive artificial pozzolan.⁶ Metakaolin is capable of reacting with portlandite to form supplementary calcium-silicate-hydrate similar in composition and structure to that generated by the hydration of portland cement.⁷

This article reports on a study to evaluate the contribution of alumina oxides from SCMs and their role in controlling expansion due to ASR. Accelerated mortar bar tests were performed that incorporated five sources of fly ash. An alumina powder ternary blend or a metakaolin ternary blend (both with fly ash and portland cement) were investigated in an attempt to increase the performance of fly ashes that previously displayed poor performance. The results showed that blends containing an overall higher level of alumina consistently performed better in ASR expansion mitigation when analyzed by the AMBT test method.

2.2 MATERIALS AND EXPERIMENTAL PROCEDURE

2.2.1 Materials

Materials used for this project were selected to ensure a specific range of chemical constituents. The chemical composition as determined by an independent testing laboratory of the high alkali ASTM C 150 Type I cement, fly ashes, and metakaolin used

are presented in Table 2-1. Properties provided by the manufacturer for the aluminum oxide powder used to augment the fly ash are listed in Table 2-2. The fine aggregate used was chosen to account for high reactivity as previously determined by the AMBT test method and is composed of natural volcanic sand.

Table 2-1. Fly ash, metakaolin, and portland cement composition.

Constituents (Wt%, dry basis)	FA1	FA2	FA3	FA4	FA5	MK	Cement
Silicon Dioxide, SiO ₂	47.66	33.70	53.15	63.95	59.36	51.11	20.08
Aluminum Oxide, Al ₂ O ₃	21.58	16.97	16.84	16.54	25.14	45.71	5.61
Iron Oxide, Fe ₂ O ₃	4.21	4.89	6.13	4.43	5.56	0.39	2.51
Total (SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃)	73.45	55.56	76.12	84.92	90.06	97.21	28.20
Calcium Oxide, CaO	12.30	27.08	11.33	6.16	5.63	0.01	63.79
Magnesium Oxide, MgO	2.70	4.63	3.93	2.38	0.94	0.00	1.22
Sodium Oxide, Na ₂ O	6.02	4.81	3.34	2.31	0.40	0.29	0.13
Potassium Oxide, K ₂ O	0.89	0.79	1.99	1.47	0.97	0.18	1.00
Na ₂ O _{eq} ^a	6.61	5.33	4.65	3.28	1.04	0.41	0.79
Titanium Dioxide, TiO ₂	0.97	1.13	1.08	0.90	1.09	1.69	0.24
Manganese Dioxide, MnO ₂	0.02	0.05	0.10	0.05	0.08	0.00	0.05
Phosphorus Pentoxide, P ₂ O ₅	0.47	0.48	0.31	0.30	0.03	0.07	0.29
Strontium Oxide, SrO	0.42	0.60	0.33	0.21	0.11	0.01	0.09
Barium Oxide, BaO	0.80	1.12	0.56	0.46	0.16	0.02	0.02
Sulfur Trioxide, SO ₃	1.20	2.92	0.64	0.54	0.37	0.08	3.39
Loss on Ignition	0.76	0.83	0.27	0.31	0.16	0.44	1.59
Moisture, as received	0.09	0.03	0.04	0.04	0.04	0.28	
Available Na ₂ O ^b	1.93	3.15	1.08	0.95	0.15	0.09	0.12
Available K ₂ O ^b	0.29	0.49	0.49	0.52	0.31	0.00	0.71
Available Na ₂ O _{eq} ^a	2.12	3.47	1.40	1.29	0.35	0.09	0.59
C ₃ S							56.20
C ₃ A							10.61
C ₂ S							15.17
C ₄ AF							7.64

^a Total alkalis (Na₂O+0.658K₂O)

^b Available alkalis, as per ASTM C311

Table 2-2. Properties of aluminum oxide powder.

Assay (Al_2O_3)	99.6
Loss of Ignition	0.2
Chloride (Cl)	0.005
Sulfate (SO_4)	<0.003
Heavy Metals	<0.0005
Iron (Fe)	<0.01

2.2.2 Experimental Methods

ASTM C 1567 (AMBT plus SCMs for mitigation) was utilized as it has been proven to be a functional method for determining the effectiveness of SCMs to mitigate expansion due to alkali-silica reaction.⁸ Length change is recorded to the nearest 0.002 mm and results are presented for the average of three or four mortar bars to the nearest 0.01%⁹ and compared to an expansion limit of 0.10% after 14 days.¹⁰

For this investigation, a control mixture and four cement-fly ash blends were cast that had replacement levels of cement with fly ash of 0%, 25%, 35% and 45%. Expansions at 14-days were recorded and two cement-fly ash systems were considered to show poor performance. These two systems were then augmented with aluminum oxide powder to increase their overall alumina content of the fly ashes to 20% or 25% and then tested again at cement replacement levels of 25% and 35%. After 14 days, the expansion of these mortar bars was compared to the expansions observed using the virgin fly ashes. The adjusted properties of the fly ashes augmented with alumina oxide powder are listed in Table 2-3.

Table 2-3. Mixture proportions and composition of FA2 augmented with aluminum oxide (%).

	FA2	FA2 at 20% Alumina	FA2 at 25% Alumina	FA3	FA3 at 20% Alumina	FA3 at 25% Alumina
Aluminum Oxide (Al_2O_3)	16.97	20.00	25.00	16.84	20.00	25.00
Silicon Dioxide (SiO_2)	33.70	32.47	30.44	53.15	51.13	47.93
Calcium Oxide (CaO)	27.08	26.09	24.46	11.33	10.90	10.22
Sodium Oxide (Na_2O)	4.81	4.63	4.34	3.35	3.21	3.01
Potassium Oxide (K_2O)	0.79	0.76	0.71	1.99	1.91	1.79
Available alkalies (Na_2O)	3.15	3.04	2.85	1.08	1.04	0.97
Available alkalies (K_2O)	0.49	0.47	0.44	0.49	0.47	0.44
Total alkalies ($\text{Na}_2\text{O}_{\text{eq}}$)	3.47	3.34	3.13	1.40	1.35	1.26

For investigating metakaolin, 5% or 10% of the least effective virgin fly ash in terms of expansion reduction was replaced with metakaolin to create ternary blends for overall replacement of cement of 5%, 10%, 15% and 25%. The mixture proportions for these ternary blends are listed in Table 2-4.

Table 2-4. Mixture proportions of blends containing FA2 and metakaolin.

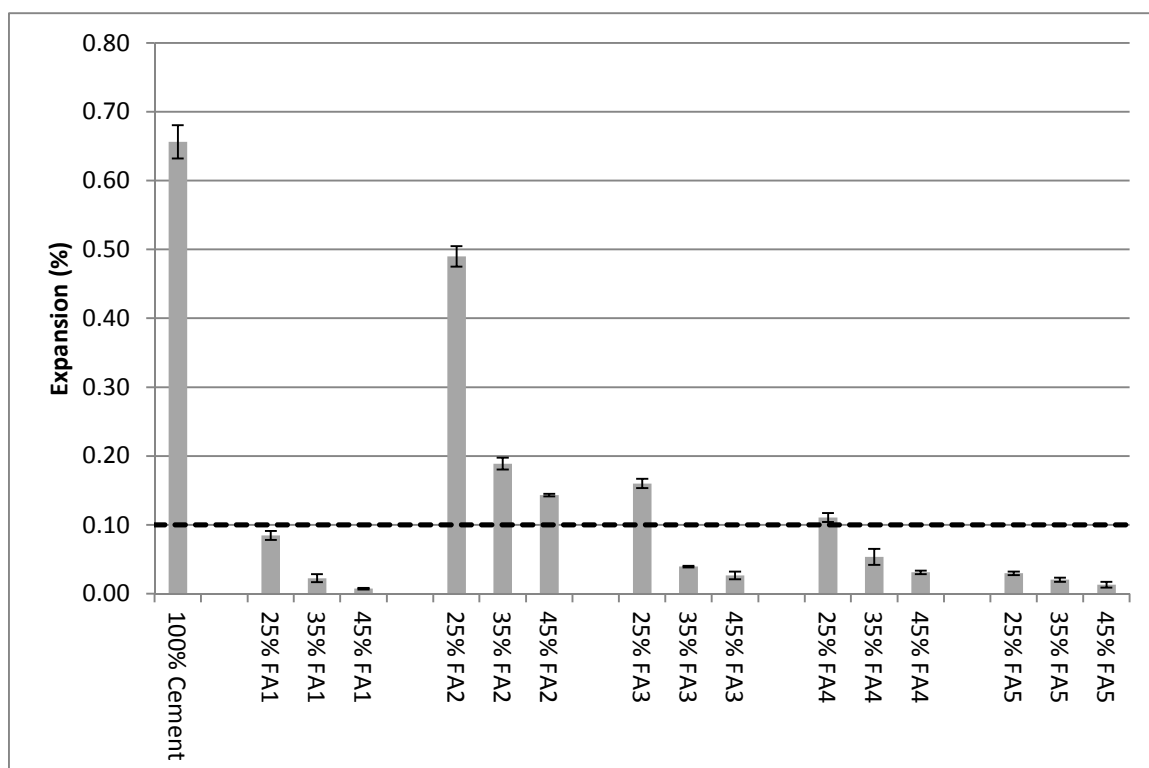
	Percent Replacement of Cement (%)	Total Mass of Fly Ash (g)	Total Mass of Metakaolin (g)	Total Mass of Cement (g)
35% FA2	35	205.33	0.00	381.34
45% FA2	45	264.00	0.00	322.67
5% Metakaolin	5	0.00	29.33	557.34
5% Metakaolin and 10% FA2	15	58.67	29.33	498.67
10% Metakaolin	10	0.00	58.67	528.00
10% Metakaolin and 15% FA2	25	88.00	58.67	440.00

2.3 RESULTS AND DISCUSSION

2.3.1 Accelerated Mortar Bar Test (AMBT) Results

Expansion of mortar bar specimens containing fly ash that was replaced at levels of 0%, 25%, 35%, and 45% at 14 days for control mixtures is presented in Figure 2-1.

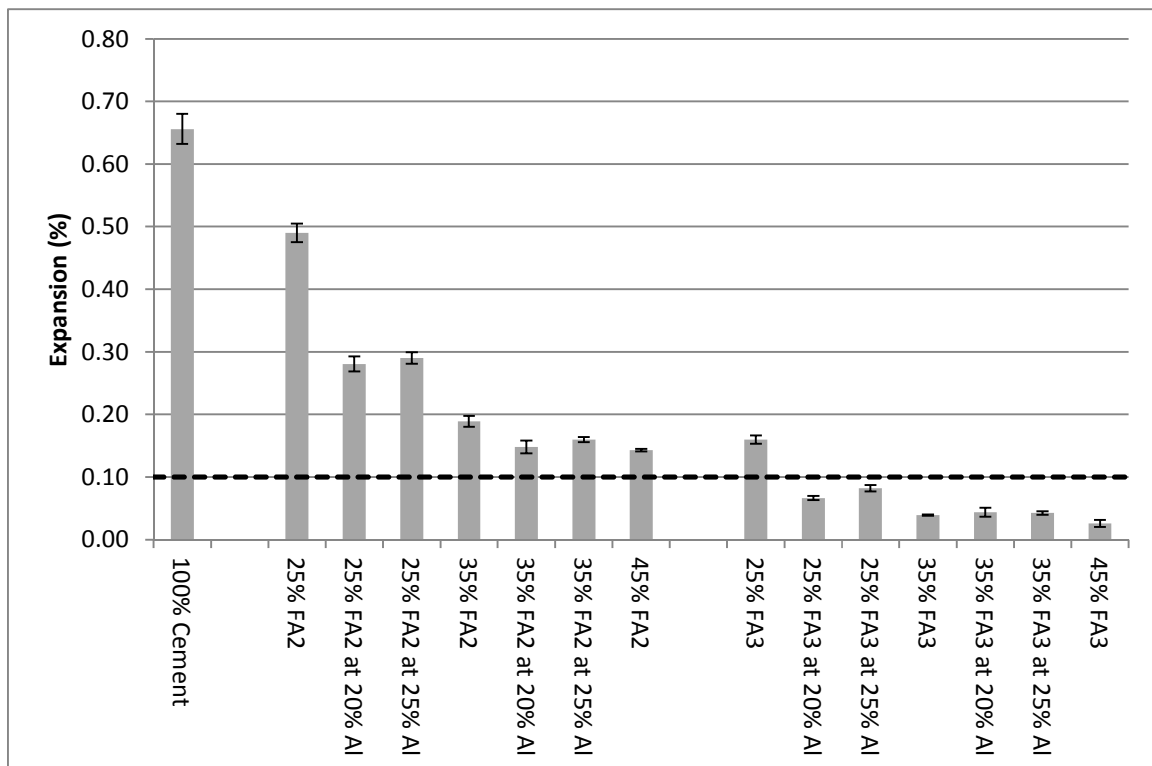
Figure 2-1. AMBT expansion results at 14 days for mortar bars containing cement supplemented with fly ash.



It can be seen that FA2 and FA3 are less effective than FA1, FA4, and FA5 at the same replacement levels. A replacement of 35% or greater was needed for FA3, whereas replacement level as high as even 45% was not effective for FA2. Additionally, FA2 and FA3 have alumina contents below 20%. FA1 and FA5 were able to control the reaction at all replacement levels and have alumina contents above 20%.

Figure 2-2 displays the 14-day AMBT expansion data for mortar bars containing FA2 and FA3 that have been augmented with alumina oxide powder to increase their overall alumina content to 20% and 25%.

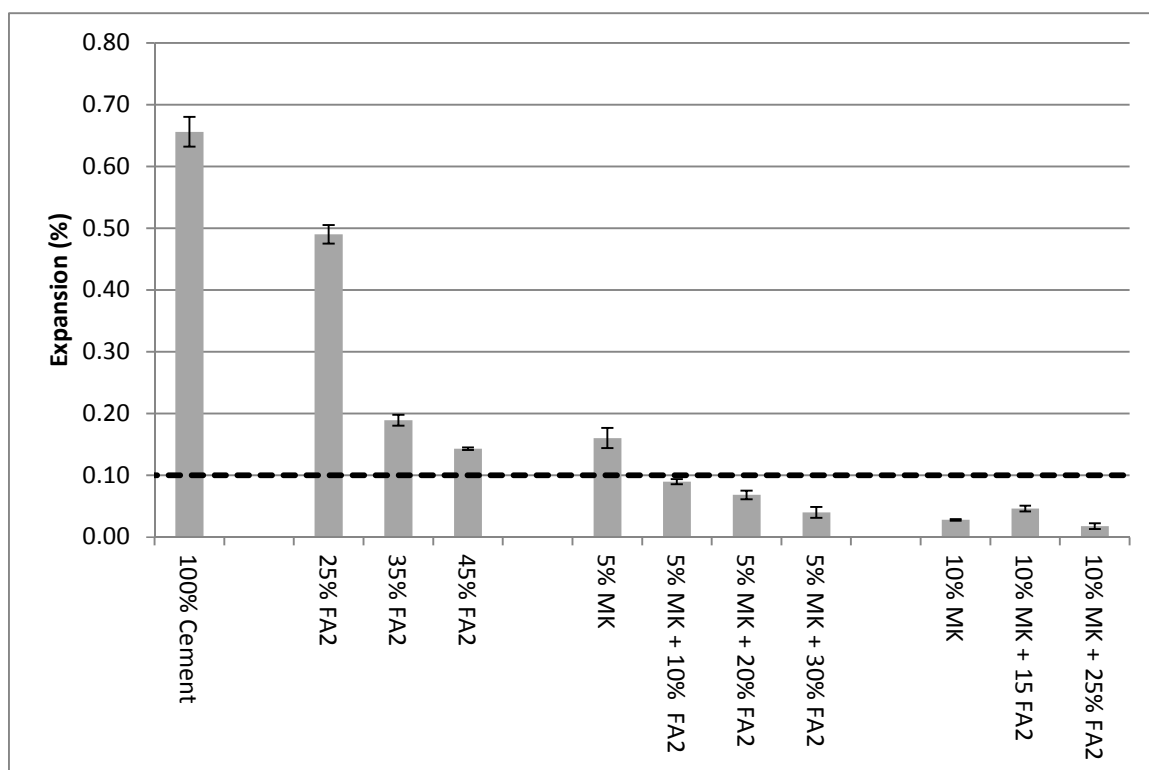
Figure 2-2. AMBT expansion at 14 days for mortar bars containing FA2 and FA3 that has alumina contents augmented to 20% and 25%.



Although all of the mortar bars containing FA2 exceed the limit of 0.10% at 14 days, a reduction is seen for all blends containing fly ash that has been augmented with alumina oxide powder.

The expansion at 14 days of mortar bar specimens for mixtures that have a percentage of virgin fly ash replaced with metakaolin to create binary and ternary blends is presented in Figure 2-3.

Figure 2-3. AMBT expansion at 14 days for mortar bars containing binary and ternary blends of FA2 and metakaolin.



It is interesting to note that a replacement of only 5% metakaolin, which contains a considerably higher amount of alumina, reduced the expansion by 65% from 0.66% to 0.14%. Although this does not pass the 0.10% expansion limit, having such a reduction in expansion with only 5% replacement of cement is significant. The expansion limit of 0.10% was not exceeded for any of the blends that contained both fly ash and metakaolin provided that 5% of the blend was made up of metakaolin.

2.4 DISCUSSION

As evidenced in the AMBT results, the addition of SCMs as a replacement of cement in binary and ternary blends can result in reduction in ASR-induced expansion. While both fly ash and metakaolin reduced expansion, metakaolin displayed greater effectiveness when used at lower rates of cement replacement than fly ash. The influence of alumina content was evident in binary and ternary blends, where expansion decreased when the alumina content of the original fly ash was increased. When the oxide levels of the fly ashes were compared, as presented in Table 2-1, a correlation was noticed between expansion and alumina content. Although FA4 exhibits similar alumina content to FA2 and FA3, it was not used in continued investigation beyond the control mixtures because of its ability to reduce expansion to an acceptable level of less than 0.10% at 14 days. Previous research would state that this is true due to its lower calcium content.¹¹ However, if that was the primary factor for forecasting the efficacy of a fly ash, then FA1 should exhibit poor performance. On the other hand, FA1 had a calcium oxide level higher than FA3 coupled with a comparably higher alumina content to the other fly ashes and exhibited some of the best results. The objective from this point was to analyze FA2 and FA3 and determine if an alteration in their chemical composition, particularly an increase in alumina, would improve their performance.

The greater relative effectiveness of fly ashes that contain higher amounts of alumina and metakaolin may be related to their elevated alumino-siliceous chemical composition. Mechanisms such as the alteration in the alkali adsorption capacity of the paste fraction and alkali activation of pozzolanic SCMs may contribute to the reduction in expansion.¹² It is still unclear which solid phase or phases of the concrete matrix may be responsible for binding alkalis. In the past, suggestion has been given to calcium silicate hydrate (C-S-H), the most copious phase in paste. Additionally, an increase in

alkali binding has been seen to be responsive to the reduction of the Ca/Si ratio of the gel. Hong and Glasser (1999) suggested that alkalis can be bound into C-S-H at acidic silanol, Si-OH, sites. It has been further suggested that alkali binding can be intensified through the incorporation of tetrahedral Al into C-S-H which results in acidity at those sites. When physically dispersed into C-S-H, alumina reacts slowly to form C-A-S-H. With further dispersion into solid solution, the alkali sorption potential increases. The mechanism proposed by Hong and Glasser suggests that Al replaces Si at tetrahedral sites creating a negative charge region that that may be capable of binding a positively charged alkali ion.^{13, 14}

A second mechanism that may be responsible for alkali sorption is borrowed from research related to alkali activated fly ash concrete (concrete without cement). The process involves geopolymerization development between a material rich in aluminosilicate oxides and an alkali solution under highly alkaline conditions. According to Glukhovsky, breakdown of the covalent bonds Si-O-Si occurs when the pH of the alkaline solution is raised. An accumulation of the destroyed products forms a gel-like structure and the generation of a condensed structure. This gel is the primary structure that results in ASR gel expansion. When alumina is present, geopolymerization results from condensation and cross linking of –Si-O-Al-O silicate links into a three dimensional network.¹⁵ The structure type of this geopolymer framework would be made up of [SiO₄] and [AlO₄] tetrahedral molecules. Similar to C-A-S-H, the incorporation of tetrahedral Al may result in an acidic location that would be charged balanced by the adsorption of alkali ions. Unlike the C-S-H phases, where structural details are based on crystal structure, details of geopolymer formation in the binder phase are particularly unidentified.¹⁶

In parallel to this possible geopolymer gel formation, the presence of calcium and the corresponding development of C-S-H and C-A-S-H results in water deficiency and a rise in alkalinity. The increased alkalinity accelerates the dissolution of silicate and aluminate species which in turn increases the rate of poly-condensation and geopolymerization. As a result, the presence of calcium contributes to the mechanical strength of the resulting hardened matrix not only by forming C-S-H and C-A-S-H, but also by enhancing the geopolymerization process.¹⁷ However, the geopolymerization and binding of alkalis is limited by the availability of Al to form tetrahedral bonds and cross linking of -Si-O-Al-O- silicate links into a three dimensional network. Figure 2-4 shows how the geopolymer and C-A-S-H development may occur within the concrete matrix.

A final mechanism to possibly describe the role of alumina in ASR expansion mitigation is its ability to lower the rate of dissolution of silica into solution. The availability of dissolved alumina has been found to hinder silica dissolution by the sorption of dissolved alumina onto silica particles in geopolymer gel formation.¹⁹ It is unclear if this would apply to alumina adsorbing to the surfaces of damaged siliceous reactive aggregate or to coagulated species of dissolved silica around the aggregate or in the pore solution. In either case, it is believed that the presence of alumina may play a role in slowing down or even blocking the rate of silica dissolution. A major factor in the ability of alumina to hinder the dissolution of silica is directly related to its rate of participation in the network. From the data in this study, it appears that the alumina is contributed at a rapid rate by the SCMs that were used. In other words, the impact of alumina content in a blend is noticeable within the 14 days of AMBT test method. Whether this impacts the service life of a structure long term is another question since the driving forces of ASR may be capable of overcoming the initial suppressive nature of alumina on silica dissolution.

From this initial research it appears that the most favorable alumina content for the fly ashes that have been augmented with alumina powder should be around 20% (or greater) since a further increase in alumina does not produce further reduction in expansion. It is unclear if the form of the alumina from the powder properly simulates the alumina contained by the fly ashes and if it is working with similar mechanics to reducing ASR expansion. Due to this uncertainty an alternative source of alumina, in this case metakaolin, was obtained to evaluate other ternary blends. The incorporation of alumina powder or metakaolin both improved the expansive mitigation potential of the fly ashes when ternary blends were utilized. This shows that fly ashes that were once deemed unusable for ASR expansion mitigation may be supplemented with other

materials to increase the effectiveness. This could result in a large impact on the use of fly ash as an SCM because it would allow a greater range of fly ashes to be used. This would decrease the amount diverted to landfills and possibly also increase its use in areas where superior fly ashes are not readily/locally available.

2.5 CONCLUSION

Binary and ternary blends of fly ash with alumina oxide powder or metakaolin were examined for their ability to resist expansion by ASR using the AMBT while incorporating a highly reactive aggregate. It was determined that alumina plays a role in the mitigation of alkali-silica reaction in the following ways:

- Results showed that alumina contributed from alumina oxide powder correlates to lower expansion. An alumina content of 20% or higher is recommended when fly ash is used to mitigate ASR expansion based on the results of this study.
- The two types of ternary blends, high-alkali portland cement with fly ash and alumina powder, and high-alkali portland cement with fly ash and metakaolin, show that higher alumina content improved mitigation of ASR expansion.
- Metakaolin displayed an increased ability to suppress ASR expansion due to its primarily alumino-siliceous composition. Lower levels of metakaolin were needed to control expansion below 0.10% in this study when compared to the amount of fly ash required to achieve the same result.
- Artificially increasing the alumina content of a fly ash through the incorporation of alumina oxide powder or metakaolin improved the effectiveness of certain fly ashes in this study to mitigate ASR expansion.

- The degree at which alumina is available when contributed by SCMs may play a role in suppressing the dissolution of silica into solution from reactive aggregates potentially delaying the rate of ASR gel formation.
- Analysis of pore solution to evaluate the efficacy of blends containing a range of alumina to bind alkalis should be conducted.

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3 SECOND MANUSCRIPT: THE EFFICACY OF HIGH ALUMINA SCMS TO CONTROL ASR

Skyler Warner, Jason H. Ideker

3.1 INTRODUCTION

Alkali-silica reaction (ASR) is an internal chemical reaction in concrete that has resulted in premature deterioration of various concrete structures worldwide. The reaction is driven by a high pH in the pore solution of the concrete.¹ The presence of alkalis from Na_2O and K_2O produces an increased pH by disassociating in solution causing positively-charged Na^+ and K^+ to be balanced by negatively charged OH^- ions. The reaction is also dependent on the presence of reactive silica. An aggregate is typically considered expansive if mortar bar expansion containing the aggregate is greater than 0.10% at 14 days in accordance to ASTM C1260/1567.² The increase in $[\text{OH}^-]$ initiates an attack on the reactive silica that causes the dissolution of silicate species. A coagulation of this silicate species with the alkali ions and lesser amounts of calcium produces a gel-like material that absorbs water resulting in expansion that generates tension in the concrete.³ Previous studies have stated that the variable chemistry of this alkali-silica gel (ASG) is characterized by the dominance of Si^{4+} , with minor amounts of Ca^{2+} , Na^+ , and/or K^+ .^{4,5} Elimination of one of the three conditions for ASR (sufficient alkalis, reactive silica, and adequate moisture) will eliminate deleterious ASR.

The use of supplementary cementitious materials (SCMs) has become the most common mitigation strategy for suppressing expansion due to ASR. The efficacy of SCMs to mitigate ASR expansion has been associated with their ability to lower the concentration of alkalis in the concrete pore solution, consequently reducing the pH and OH^-

concentration.⁶⁻⁸ This is likely due to an alteration of the hydration product calcium-silicate-hydrate (C-S-H), the most copious hydration product for all portland cement systems. For systems containing SCMs, the C-S-H typically has a decreased Ca/Si atomic ratio that results in an improvement in binding alkalis from the pore solution.⁹⁻¹¹ The removal of alkalis from the pore solution may reduce hydroxyl ion concentrations to levels low enough that ASR related expansion does not ensue.

Currently, the most common mitigation strategy involves the use of fly ash, a byproduct of coal combustion that would otherwise be landfilled. The morphological properties affected by fly ash production and its chemical composition have a direct effect on its ability to control ASR.^{6, 7, 12-14} Fly ash is often preferred due to its ability to improve workability as well as increase strength and long-term performance of hardened concrete. Particular fly ashes used at replacement levels of up to 40% have been found effective in significantly reducing expansion and cracking of hardened concrete associated with ASR¹⁵. However, variability in fly ash properties (due to combustion, collection processes, and differing sources of coal) and some unfavorable properties at higher replacement levels, such as delayed set times, have limited its use as a replacement for portland cement in amounts higher than the industry-typical 30% replacement levels.¹²

There are three main characteristics that attribute to the effectiveness by which fly ash can mitigate ASR expansion: fineness, mineralogy, and chemistry. The use of finer pozzolans creates a denser material that reduces the permeability of the matrix and penetration of water into the system. It also provides enhanced surface area that can increase the potential for the pozzolanic reaction to form additional beneficial hydrate products such as C-S-H. An optimum mineralogy of the fly ash will provide chemical

components that can combine with cementitious hydrates to effectively bind alkalis and/or are able to chemically react with the other constituents.^{6, 7, 14, 16, 17}

Metakaolin is a material that may be suitable on its own or as a complement to fly ash for the purpose of ASR damage mitigation when used in a ternary blend (portland cement with partial replacements of two SCM materials). Made up of primarily alumina and silica oxides, metakaolin is manufactured under a carefully controlled process by thermally activating purified kaolinite clay within a specific temperature range (650-800°C). The resulting anhydrous alumino-silicate ($\text{Al}_2\text{Si}_2\text{O}_7$) is mainly amorphous material that behaves as a highly reactive artificial pozzolan¹⁸. Malquori¹⁹ and Turrizani²⁰, and more recently DeSilva²¹ et al., have discussed the chemical reactions involved when calcined clays are used as pozzolans for concrete. In the presence of water, the primary reaction occurs between the alumino-silicate products of the metakaolin and the calcium hydroxide developed from cement hydration.²² The high degree of reaction of metakaolin results in long-chain highly aluminous C-S-H, or C-A-S-H, where most of the bridging sites are occupied by Al^{3+} rather than the traditional Si^{4+} and the incorporation of alumina into hydration products has been found to enhance alkali binding.²³⁻²⁵ Other crystalline products include calcium aluminate and alumino-silicate hydrates (i.e., C_2ASH_8 , C_4AH_{13} and C_3AH_6)²⁶⁻²⁸. Metakaolin also influences the microstructure and diffusion properties of blended cement pastes and concrete.²⁸⁻³¹ Blended pastes containing metakaolin possess a finer pore structure compared to plain cement pastes³⁰ as well as a reduced rate of diffusion of Na^+ ions and rate of water absorption.^{28, 29}

It is known that for metakaolin, when immersed in an alkaline solution, an attack on the structure occurs that results in the release of silicate and aluminate species into solution

and the alumina is converted to a primarily 4-coordination.³² The formation of 4-coordination alumina, Al[4], may be essential for the binding of alkalis from solution during the formation of C-A-S-H. While it has also been shown that both Al[4] and Al[6] arise in the C-S-H of ordinary cement systems and alumina can also occur in both ettringite (AFt) and monosulfate (AFm) of such systems^{33, 34}, it is believed that Al[4] is desired for alkali binding.

The structural mechanism for which alumina may substitute for silica in the C-S-H of fly ash and metakaolin based cements has been studied but still remains a topic of considerable discussion.^{35, 36} Many of the studies have been performed on synthetically produced C-S-H and C-A-S-H rather than actual cement-based systems. It was first suggested by Kalousek³⁷ when analyzing tobermorite, the structural model for many C-S-H samples, that alumina may substitute for silica primarily in the tetrahedral sites and recent studies have improved the understanding of the role of alumina in C-S-H and its model compounds, tobermorite and jennite.^{33, 38-43} It was later revealed that tetrahedrally coordinated alumina may affect cation exchange properties by occurring across interlayers.^{31, 38-40} Lognot et al.⁴⁴ confirmed that Al[4] may occur in precipitated C-S-H in both the bridging and pairing tetrahedra of the chains and that alkalis participate in charge balancing the Al[4] for Si[4] substitution.

In an effort to determine how alumina contributes to reducing expansion due to ASR, several different tests were performed. A sequence of ASTM C1567 accelerated mortar bar tests (AMBT) were conducted to investigate how an increase in alumina content could correspond to a reduction in expansion due to ASR. Pore solution chemistry of the cementitious systems tested by AMBT were then compared to their expansions. The investigation was concluded in an attempt to determine if increased amounts of

alumina would result in the development of alkali binding structures using Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA), and X-ray Diffraction (XRD).

3.2 MATERIALS AND EXPERIMENTAL PROCEDURE

3.2.1 Materials

A high alkali ASTM C150 Type I/II cement was selected for this study. The aggregate used was a highly reactive natural siliceous sand from the Willamette Valley, Oregon USA. Of the fly ashes used, two fly ashes were shown to be impractical mitigation options according to ASTM C1567, one was considered to be a “borderline fly ash” in terms of its effectiveness and the other was considered to be ineffective in controlling ASR at standard dosage rates (e.g. 15-35%).⁴⁵ The majority of this study focused on improving the efficacy of the borderline and ineffective fly ashes. These two fly ashes had similar alumina content and considerable variation in oxide content was attributed to their calcium and alkali contents. In order to elevate the alumina content of the fly ashes, 98.5% alumina oxide powder was used. The metakaolin chosen, manufactured by Thiele Kaolin Company from Georgia, USA, contained a higher amount of alumina compared to the two fly ashes as well as trace amounts of calcium and alkalis. Table 3-1 displays the oxide analysis for the chemical constituents of the materials used as determined by an independent testing laboratory.

Table 3-1. Chemical composition of materials (mass %)

Constituent (Wt%, dry basis)	High Alkali Cement	FA1	FA2	FA3	FA4	Metakaolin	Ultra-Fine Fly Ash
SiO ₂	20.30	47.39	33.70	53.14	64.77	51.11	53.04
Al ₂ O ₃	5.37	21.99	16.97	16.84	16.10	45.71	26.53
Fe ₂ O ₃	2.02	4.19	4.89	6.13	4.63	0.39	4.65
SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃	27.69	73.56	55.56	76.12	85.50	91.21	84.22
CaO	63.36	12.27	27.08	11.33	5.87	0.01	8.88
MgO	1.74	2.44	4.63	3.93	2.19	0.00	1.86
Na ₂ O	0.09	6.15	4.81	3.34	2.19	0.29	0.44
K ₂ O	1.24	0.88	0.79	1.99	1.49	0.18	1.19
Na ₂ O ^b	0.91	6.73	5.33	4.65	3.17	0.41	1.22
TiO ₂	0.27	1.01	1.13	1.08	0.91	1.69	1.44
MnO ₂	0.07	0.01	0.05	0.10	0.05	0.00	0.07
P ₂ O ₅	0.03	0.44	0.48	0.31	0.24	0.07	0.26
SrO	0.08	0.46	0.60	0.33	0.21	0.01	0.11
BaO	0.04	0.79	1.12	0.56	0.47	0.02	0.11
SO ₃	3.71	1.19	2.92	0.64	0.49	0.08	0.94
LOI	1.68	0.79	0.83	0.27	0.39	0.44	0.48
Moisture	0.68	0.05	0.03	0.04	0.08	0.28	0.19
Na ₂ O ^a	0.13	2.64	3.15	1.08	0.85	0.09	0.20
K ₂ O ^a	0.80	0.26	0.49	0.49	0.45	0.00	0.36
C ₃ A	10.82						
C ₂ S	17.38						
C ₃ S	54.11						
C ₄ AF	6.15						

^aAvailable alkalis, as per ASTM C311^bTotal alkalis (Na₂O+0.658K₂O)

3.2.2 Experimental Procedures

3.2.2.1 Accelerated Mortar Bar Test (ASTM C1567)

A sequence of ASTM C1567 (Standard test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate) accelerated mortar bar tests (AMBT) were conducted with varying ranges of chemical constituents to assess the ability of fly ashes to mitigate ASR. ASTM C 1567 (AMBT) is a modification

of ASTM C 1260 where a specific percentage of cement is replaced with SCM material. The standard recommends testing the same aggregate and hydraulic cement without pozzolans or slag using Test Method C 1260. SCMs may be tested together or individually in binary or ternary blends to determine a combination of constituents required to reduce expansion to a specified value (also generally 0.10% at 14 days).⁴⁶ A high range water reducer (HRWR) may be used if necessary when testing blends containing silica fume or metakaolin and the water-cementitious ratio must remain at 0.47 by mass⁴⁷, however no HRWRs were used in this investigation. Mortar prisms were cast that measure 1 in. x 1 in. x 11.25 in (25 mm x 25 mm x 285 mm). An effective gage length of 10.00 ± 0.10 in. (250 ± 2.5 mm) was created by casting a stainless steel gage stud into each end of the mortar bars. For the initial 24 ± 2 hours, the bars were cured in a 100% relative humidity room at 73.4 ± 3 °F (23 ± 1.7 °C). The bars were then removed from the molds, measured and submerged in tap water. From this point on and for the remainder of the test, the bars were placed in an oven at 176 ± 3.6 °F (80.0 ± 2.0 °C). The initial or zero reading of the bars was taken 24 ± 2 h from placement in the tap water when the bars were then quickly transferred to a solution of 1N NaOH that was previously prepared and brought to 176 ± 3.6 °F (80.0 ± 2.0 °C) for 14 days. Length measurements were taken during the 14 day time period during the ± 2 h time window that the zero reading was previously taken. Length change was recorded to the nearest 0.0001 inch and presented to the nearest 0.01% for the average of a minimum of three mortar bar prisms.⁴⁸

3.2.2.2 Alumina augmentation

Aluminum oxide powder, 99.6% Al_2O_3 , produced by J.T. Baker was supplemented into particular blends in order to analyze if the direct incorporation of alumina into a system

could improve the performance of fly ash to control alkali-silica reactive aggregates subjected to ASTM C 1567. The alumina oxide powder was treated as a cementitious material. When incorporated into a blend to increase the alumina content of a fly ash, the powder replaced a portion of fly ash in order to keep the total replacement of portland cement consistent.

3.2.2.3 Pore solution analysis

Emission spectroscopy can be utilized for the determination of trace or ultratrace elements. The technique accepts liquid samples which are vaporized using an arc discharge, spark, or plasma. Stable plasmas are supported by the inductive coupling of the hot cloud of ionized gas to an electrically driven radio-frequency coil, hence the further development of inductively coupled plasma (ICP). ICP is proficient for the analysis of liquid samples that are directly injected into the plasma. The concentration of various cations can be measured directly and simultaneously with high sensitivities by atomic emission (ICP-AES).¹³

The pore solution analysis involved binary blends of FA2 or metakaolin and ternary blends of FA2 with alumina oxide powder or metakaolin. Additionally, blends incorporating 2 and 5% alumina oxide powder replacing portland cement by mass were also analyzed to investigate the impact of a pure alumina source. The replacement amounts of 2 and 5% were similar amounts of alumina that were incorporated into the systems involving 5 and 10% metakaolin.

Pastes were mixed in a 3-speed mixer following ASTM C 305.⁴⁹ After mixing, the samples were rotated around a horizontal axis for 24 hours to prevent bleeding. The samples were stored at either 23°C, as a benchmark temperature, or 80°C to accelerate

chemical reactions, especially the release of alkalis for 1, 7, 14, 28 or 90 days to assess hydration progression. Pore solution extraction was performed after crushing the paste samples to pieces smaller than 20mm in any dimension and placed into a hardened steel pore press and a maximum force of at least 250,000 lbs (~63,000 psi, 434 MPa) was applied at a rate of 300-400 lbs/sec. Pore solution was collected at the bottom of the press in a 6 mL vial. Within 2 hours of collection, pH readings were determined by a Thermo Scientific Orion Star Plus pH meter. Chemical analysis was subsequently performed using an inductively coupled plasma atomic emission spectrometer (ICP-AES Perkin-Elmer Optima 5300).

3.2.2.4 Thermal Analysis (DTA/TGA)

Differential thermal analysis (DTA) identifies the thermal decomposition of different phases of a paste sample, in this research measured by TA Instruments 1600 DTA. Thermogravimetric analysis (TGA) measures the change in mass due to decomposition, in this research measured by TA Instruments Q500 TGA. Pastes were mixed in a 3-speed mixer following the mixing instructions set forth by ASTM C 305.⁴⁹ After mixing, the samples were rotated around a horizontal axis for 24 hours to prevent bleeding. The samples were stored at 80°C to accelerate hydration for 28 days. Prior to testing, the samples were crushed to small pieces (approximately 0.05mm to 0.2mm in size) from which a portion was ground using mortar and pestle until particles were able to pass a 200 sieve. Specimens were decomposed in platinum crucibles at a temperature range from 23 to 1100°C at a rate of 10C/min in a flow of N₂ gas.

3.2.2.5 X-ray Diffraction (XRD)

For the five samples previously analyzed by TGA and DTA techniques, the powder method of X-ray diffraction was implemented using a Bruker Axs D8 Discover

Diffraction Data were used to provided phase identification for crystalline phases.⁵⁰

Paste sample for XRD analysis were created following the procedures and described in Section 2.2.4. DTA, TGA, and XRD analysis was performed on mixtures from the same batch. After being crushed to small pieces, a portion of each sample was soaked in acetone for 48 hours to halt hydration and remove exchangeable water. Samples were then placed in a vacuum desiccator to avoid carbonation for 24 hours for drying then ground using mortar and pestle until particles were able to pass a 200 sieve. Each powder sample was mixed with a titanium oxide (TiO₂) standard at a proportion of 90% sample and 10% standard in ethanol to provide semi-quantitative XRD results. The specimens were placed in the desiccator to dry again for 24 hours and then tested.

3.3 RESULTS AND DISCUSSION

3.3.1 Accelerated Mortar Bar Test (ASTM C1567)

The ASTM C1567 expansions of mortar bars containing 100% high alkali cement or 25-45% replacement of FA1, FA2, FA3 and FA4 fly ashes with a highly reactive fine aggregate are presented in Table 3-2. Values in bold correspond to expansions exceeding the 0.10% limit.

Table 3-2. ASTM C1567 expansion results for mortar bars containing 25, 35, or 45% fly ash and a highly reactive siliceous aggregate.

Fly Ash Content (%)	FA1	FA2	FA3	FA4
Control	0.66	0.66	0.66	0.66
25	0.08	0.49	0.16	0.03
35	0.02	0.19	0.04	0.02
45	0.01	0.14	0.03	0.01

FA1 and FA4 were capable of suppressing expansion below 0.10% at a replacement level of 25%. FA4, which had a much lower CaO content than FA1, performed better, supporting the idea that low calcium fly ash are more effective for controlling ASR. However, the calcium content of FA3 was slightly lower than FA1, but was not able to suppress expansion below the 0.10% limit at 14 days at a replacement level of 25%. By comparison of the alumina content, it can be seen that the alumina content of FA1 was higher than FA3, which gave rise to the idea that an increased amount of alumina may have resulted in improved effectiveness. While the alumina contents of FA2 and FA3 were similar, the SiO₂ and CaO were very different. FA2 had a much higher CaO content than FA3. According to ASTM C618, the FA1, FA2 and FA3 fly ashes would be considered class C fly ashes considering their calcium content is above the current 10.0% limit. Comparing ashes with similar CaO content, while a higher value for available alkalis exists for FA1 (2.81) than FA3 (1.40), FA1 actually shows greater effectiveness. It may indicate that the higher Al₂O₃ content of FA1 played a more significant role in controlling expansion, as will be discussed in sections to follow.

It was observed that mortar bars containing reactive fine aggregate with FA2 and FA3 fly ashes at a 25% replacement level by mass of cement exhibited expansions above the ASTM C 1567 limit of 0.10% at 14 days. Furthermore, mortar bars with increasing amounts of FA2 up to replacement levels of 45% continued to exhibit expansions above 0.10%. FA2 and FA3 contained low amounts of alumina (16.97 and 16.84) in comparison to FA1 (21.99), which passed the ASTM C 1567 test at 14-days. Due to their reduced effectiveness in suppressing expansion along with their low alumina content and distinct calcium levels, FA2 and FA3 were chosen for further study. It was postulated that increasing the alumina level in the cementitious blends by adding Al_2O_3 powder would increase their effectiveness in controlling ASR. Table 3-3 displays the resulting oxide levels for blends containing FA2 and FA3 with elevated amounts of alumina of 20% or 25%. The oxide content, (Al_2O_3 input), and total alumino-siliceous content, (Si + Al), of the binary or ternary blends considering all cementitious materials and resulting ASTM C1567 mortar bar expansions for these blends at 14 days are also presented in Table 3-3.

Table 3-3. Oxide composition of FA2 fly ash supplemented with alumina oxide powder.

Blend Description		Final Oxide Composition of Blend			Alumino-siliceous values and expansion	
		CaO input	SiO ₂ input	Al ₂ O ₃ input	Al + Si	Expansion (%)
Control		64.21	20.51	4.72	25.23	0.66
25% FA2	Original	54.93	23.81	7.78	31.59	0.49
	20% Alumina	54.68	23.50	8.54	32.04	0.28
	25% Alumina	54.27	22.99	9.79	32.78	0.29
35% FA2	Original	51.21	25.13	9.01	34.13	0.19
	20% Alumina	50.87	24.70	10.07	34.76	0.11
	25% Alumina	50.30	23.99	11.82	35.80	0.16
25% FA3	Original	50.99	28.67	7.75	36.42	0.16
	20% Alumina	50.88	28.17	8.54	36.71	0.07
	25% Alumina	50.71	27.37	9.79	37.16	0.06
35% FA3	Original	45.70	31.93	8.96	40.90	0.04
	20% Alumina	45.55	31.23	10.07	41.30	0.04
	25% Alumina	45.31	30.11	11.82	41.93	0.04

Although the incorporation of alumina oxide powder to increase the overall alumina content resulted in a reduction of SiO₂ and CaO, the classification of FA2 and FA3 remained Class C according to ASTM C618. Increasing the alumina content of a cementitious blend by the incorporation of alumina oxide (Al₂O₃) powder improved the efficacy to mitigate ASR expansion. Blends that passed the ASTM C1567 mortar bar expansion limit of 0.10% are represented as bold in Table 3-3. These blends had an overall alumino-siliceous content greater than 36.5%. All blends containing alumina oxide powder resulted in a reduction in expansion when compared to the control blend and to blends with original unaltered alumina contents. For both fly ashes at a

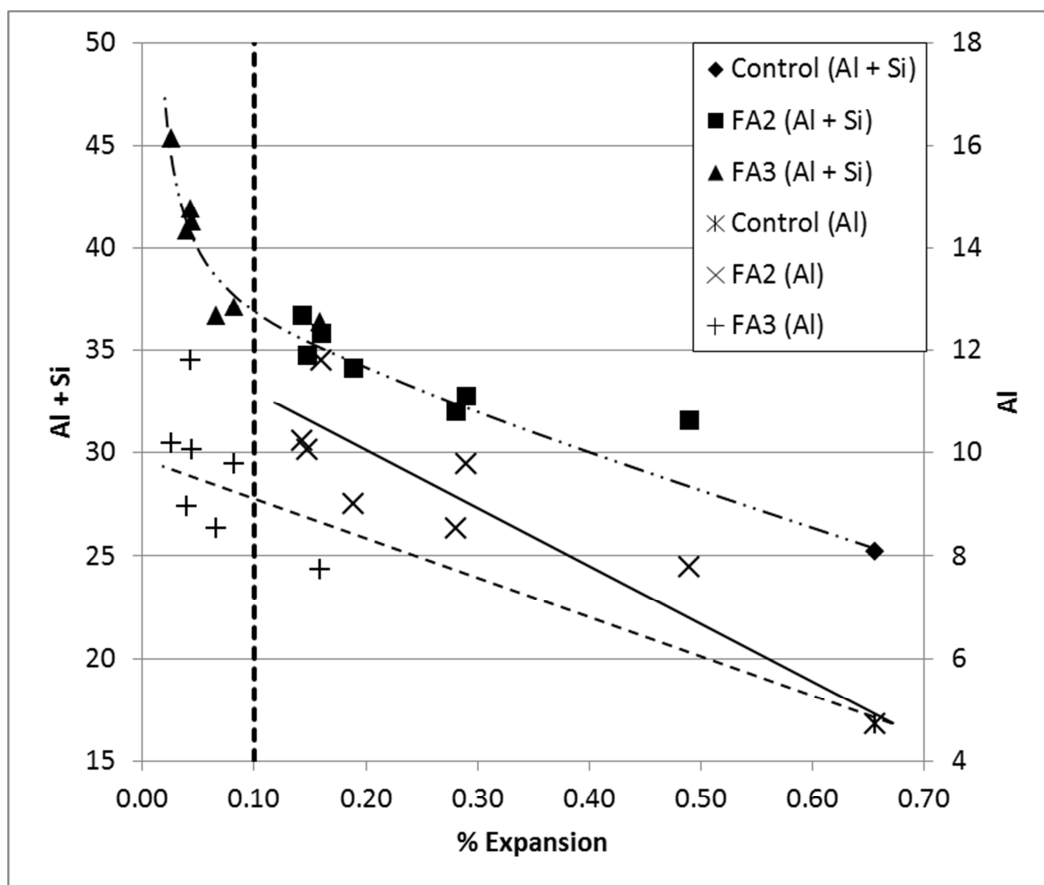
replacement level of 25%, an increase in alumina content to 20% reduced expansions but a further increase in alumina content to 25% did not display continued improvement. However, expansion was still reduced compared to the original alumina content of the blends. For a replacement of 35%, FA2 showed similar results while FA3 showed neither an improvement nor decline in reducing expansion when the alumina content was increased from 20 to 25%.

The results collected to this point support the hypothesis that higher levels of alumina in fly ash provide improved ASR mitigation. It is already well known that low calcium fly ash is preferred for the mitigation of expansion due to ASR. An alternative way to view this is that a fly ash with a considerable alumino-siliceous content, Si + Al above 70%, provides enhanced performance for the mitigation of expansion due to ASR. However, for a fly ash with a particular alumino-siliceous content, it is still not clear what fraction should be composed of alumina.

For this investigation, it is important to remember that the (Al+Si) values are a summation of oxides contributed by all of the materials, which may include ordinary portland cement, fly ash or alumina oxide powder. The control blend contained no fly ash or alumina oxide powder and as a result has the lowest (Si + Al) value. Additionally, it displayed the largest expansion of 0.66% at 14 days. The blend with the highest (Si + Al), in this case the binary blend containing 45% FA3, resulted in the lowest expansion of 0.03% at 14 days.

For the particular materials tested, it can be seen in Figure 3-1 that a general reduction in expansion occurs with an increase in (Al + Si) content.

Figure 3-1. (Al + Si) and Al contents of binder materials (cement, fly ash, and Al_2O_3 powder) and resulting ASTM C1567 14-day expansions for blends containing FA2 or FA3 augmented with alumina oxide powder.



It is not until the (Si + Al) value is above 36.5% that the expansion is lowered to the ASTM C1567 limit of 0.10% at 14 days. This validates the idea that fly ash containing lower amounts of calcium due to an elevated alumino-siliceous content should provide enhanced ability for the mitigation of ASR. Additionally, Figure 3-1 demonstrates that increasing the alumina content of a blend by the direct incorporation of alumina oxide

powder or more SCM material results in reduced expansions, which is displayed by the solid and dashed lines.

As noticed in the alumina augmentation portion, blends containing elevated (Si + Al) values coupled with a low calcium content seem to provide the best mitigation for expansion due to ASR. Since the incorporation of alumina powder as a ternary material with FA2 showed enhanced efficacy in controlling ASR for mortar bars containing highly reactive fine aggregate compared to the binary mixtures with FA2 alone, other supplementary cementitious materials with considerably higher levels of alumina (other than fly ash or alumina powder) were investigated. In particular, consideration was given to materials that were already known to provide ASR mitigation strategies. Due to its high alumino-siliceous content and very low calcium content, metakaolin was initially chosen. The test matrix and ASTM C1567 expansion results at 14 days for mortar bars containing binary blends of FA2, metakaolin or ultra-fine fly ash and ternary blends of FA2 with metakaolin or ultra-fine fly ash with a highly reactive aggregate are displayed in Table 3-4.

Table 3-4. Test matrix and ASTM C1567 expansion results at 14 days for mortar bars containing binary blends of FA2, metakaolin or ultra-fine fly ash and ternary blends of FA2 with metakaolin or ultra-fine fly ash.

Blend Description	FA2 (%)	Metakaolin (%)	UFFA (%)	% Expansion at 14 days
Control	0	0	0	0.66
FA2	25	0	0	0.49
	35	0	0	0.19
	45	0	0	0.14
5% Metakaolin + FA2	0	5	0	0.16
	10	5	0	0.09
	20	5	0	0.07
	30	5	0	0.04
10% Metakaolin + FA2	0	10	0	0.03
	5	10	0	0.04
	15	10	0	0.05
	25	10	0	0.02
5% Ultra-Fine Fly Ash	0	0	5	0.21
	0	0	15	0.01
	0	0	25	0.01
5% Ultra-Fine Fly Ash + FA2	10	0	5	0.21
	20	0	5	0.12
	30	0	5	0.08
10% Ultra-Fine Fly Ash + FA2	5	0	10	0.04
	15	0	10	0.03

Mortar bars containing highly reactive fine aggregate with binary and ternary blends of FA2 fly ash and metakaolin were cast in accordance to ASTM C1567. The purpose was to determine if the incorporation of metakaolin at various levels could improve the efficacy of blends containing fly ashes that have a high CaO and low Al₂O₃ content, such as FA2. Mortar bars with binary blends of metakaolin contained replacement of cement by mass with 5% and 10% metakaolin. Mortar bars with ternary blends contained 5%

and 10% metakaolin and enough FA2 to create an overall replacement of cement equal to 15%, 25%, or 35%.

For mortar bars containing highly reactive aggregate and a 5% replacement of cement by mass with metakaolin, the expansions were not less than the 0.10% expansion limit for ASTM C 1567 at 14-days but the blend did perform better than 25 and 35% FA2. An increased replacement level of 10% metakaolin was shown to be effective at reducing the expansion below the 0.10% limit; outperforming all binary blends supplemented with FA2. FA2 fly ash was added to 5% and 10% metakaolin to create overall replacement levels of 15%, 25%, and 35% for portland cement. For all blends containing 5% metakaolin, the addition of FA2 displayed synergy between the two products by a reduction in expansion with increasing amounts of FA2. However, blends containing 10% metakaolin were nominally less effective with the addition of 5 and 15% FA2. This trend did not continue for the blend containing 10% metakaolin with 25% FA2 for which the effectiveness was improved.

The inclusion of FA2 with metakaolin to form ternary blends demonstrated the blend's ability to suppress expansion at 14-days for all of the ternary blends tested. The inclusion of alumino-siliceous metakaolin in ternary blends with FA2 fly ash may allow for the use of such a fly ash, which on its own would not prevent deleterious ASR even up to a 45% replacement level under ASTM C 1567 testing. The replacement levels of fly ash and metakaolin may differ depending on the level of reactivity of the aggregate used. For other materials, the quality of the fly ash and metakaolin used will become factors in choosing an appropriate blend. For this mixture in which highly reactive siliceous sand was used, a blend containing high alkali cement replaced with 5% metakaolin and 10% FA2 fly ash was found to suppress expansion at 14-days. However,

higher levels of replacement, for example 5% metakaolin combined with 30% fly ash of FA2, may be considered if lowering the quantity of cement used is a project goal in conjunction with effective ASR mitigation.

The use of ultra-fine fly ash may be used in ternary blends, similarly to metakaolin, to improve the overall fineness, mineralogy, and chemistry of a blend that incorporates a fly ash that is less effective at controlling ASR such as FA2. The supplementation of 5% ultra-fine fly ash alone performed better than 25% FA2 fly ash on its own. Additionally, ultra-fine fly ash at 15% significantly outperformed binary blends with only FA2. The inclusion of FA2 fly ash with ultra-fine fly ash in ternary blends showed the ability to suppress expansion at 14-days when replacement of cement included 5% ultra-fine fly ash with 30% FA2 or 10% ultra-fine fly ash with 5% FA2. It is interesting to note that the addition of 10% FA2 to 5% ultra-fine fly ash did not produce increased effectiveness compared to the binary blend of 5% ultra-fine fly ash alone.

The results for blends containing ultra-fine fly ash presented in Table 3-4 are similar to those found for ternary blends of FA2 with metakaolin. The inclusion of a high alumina ultra-fine fly ash in ternary blends with a fly ash such as FA2 may improve the efficiency of cement systems containing SCMs to mitigate expansion due to ASR as well as reducing the total replacement level of cement for the purpose of constructability.

3.3.2 Pore Solution Analysis

For particular blends analyzed by ASTM C1567 and discussed in Section 3.1, further investigation was conducted to monitor the change in chemistry of the pore solution of hardened cement pastes when incorporating supplementary cementitious materials of varying mineralogy and chemistry. There are several aspects to consider when

determining how a material is working mechanistically to suppress ASR expansion when analyzing the pore solution. This may include lowering the level of alkalis available in the pore solution or lowering the pH of the pore solution through pozzolanic activity of SCMs.^{7, 14} Additionally, particular SCMs have shown the potential for suppressing silica dissolution from the reactive aggregate.⁵¹ As mentioned before, the primary objective of this investigation was to determine if cementitious systems with considerable amounts of alumina would exhibit improvements in the removal of hydroxyl ions or alkalis from the pore solution; two mechanisms that would assist in the mitigation of ASR. Table 3-5 displays the total alumina content by mass considering any materials involved in the blend (portland cement, fly ash, metakaolin, and/or alumina oxide powder) and resulting pH and alkali concentrations of the pore solution for samples cured at 80°C for 14 days.

Table 3-5. Binder alumina content, pH, and alkali concentration of binary blends of FA2, Al₂O₃ powder, or metakaolin or ternary blends of FA2 with alumina oxide powder or metakaolin.

Blend Description		Binder Alumina Content (% Al ₂ O ₃)	Aqueous Alumina (µg/mL)	Aqueous Potassium (µg/mL)	Aqueous Sodium (µg/mL)	pH
Control		4.72	6.33	19595	2364	12.99
FA2 only	25% FA2	0.00	7.78	13024	13.20	13.20
	45% FA2	54.00	10.23	7149	13.03	13.03
FA2 at 20% Alumina	25% FA2 at 20% Al	0.13	8.54	12284	13.11	13.11
	35% FA2 at 20% Al	8.54	10.07	7234	13.53	13.53
FA2 at 25% Alumina	25% FA2 at 25% Al	3.39	9.79	12545	13.12	13.12
	35% FA2 at 25% Al	1.10	11.82	8345	13.11	13.11
Al ₂ O ₃ Powder only	2% Al ₂ O ₃ Powder	0.05	6.62	14992	12.39	12.39
	5% Al ₂ O ₃ Powder	0.00	9.47	11844	12.28	12.28
5% MK and FA2	5% Metakaolin	7.50	6.77	13621	12.63	12.63
	5% MK + 20% FA2	2.00	9.22	8781	12.72	12.72
	5% MK + 40% FA2	99.00	11.67	5939	12.59	12.59
10% MK and FA2	10% Metakaolin	1.49	8.82	8281	12.65	12.65
	10% MK + 15% FA2	6.22	10.66	6538	7604	12.59
	10% MK + 35% FA2	102.00	13.11	3450	8284	13.38

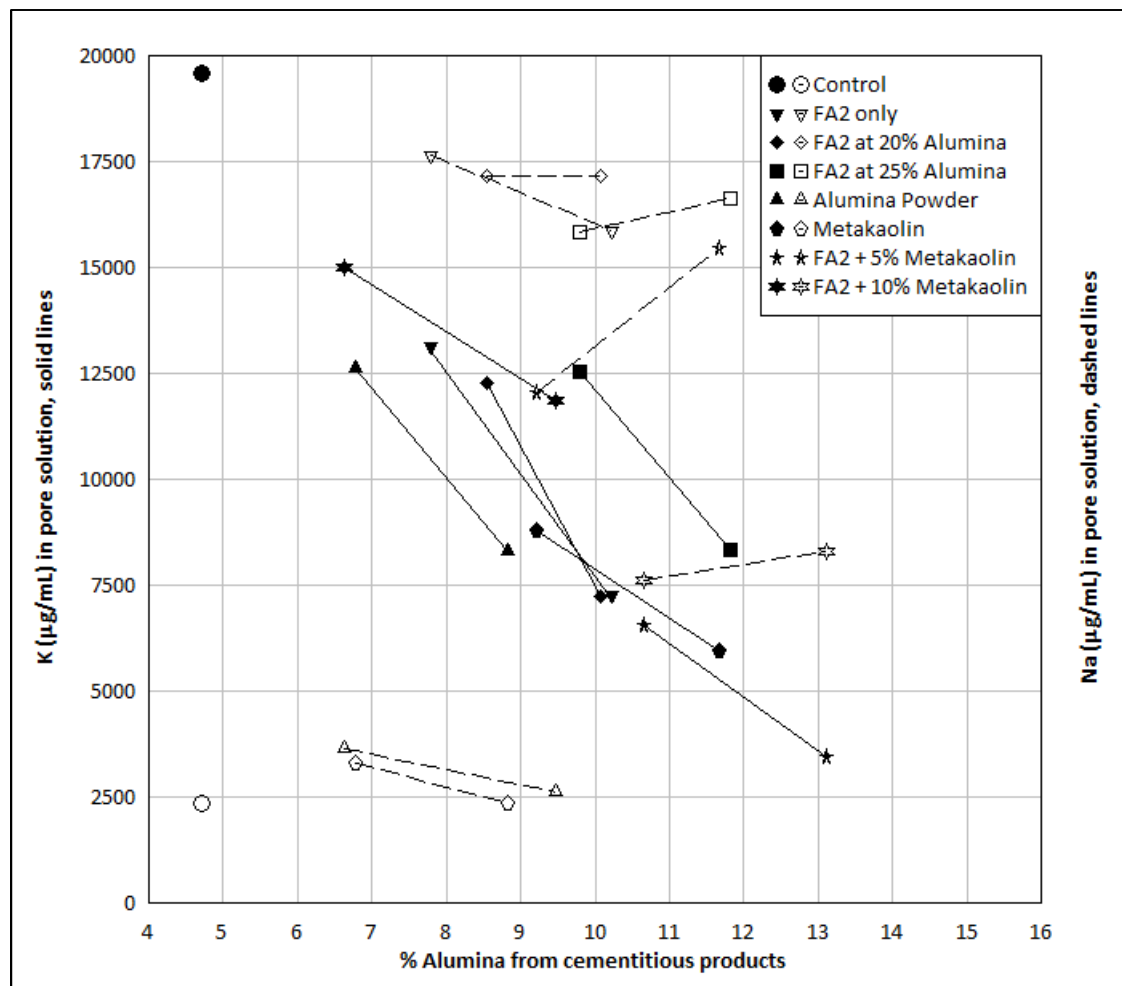
It can be seen in Table 3-5 that the control sample containing only high alkali cement had the lowest alumina content. This resulted in a pH of 12.99 and a total alkali concentration of 21959 µg/mL. Paste samples that showed a reduction in pH and total alkali concentration at 14 days compared to the control were composed of binary blends of alumina oxide powder or metakaolin as well as ternary blends of FA2 with metakaolin. Samples that resulted in an increase in pH and total alkali concentration from the control were composed of binary blends of FA2 or ternary blends incorporating FA2 with alumina oxide powder. One ternary blend of FA2 with metakaolin did have a pH above 13.0, but this sample also contained a much greater amount of FA2 (35%)

compared to metakaolin (10%). Interestingly, the samples that showed the greatest efficacy to lower the pH were the binary blends of alumina oxide powder showing that alumina may play some direct role in regulating pH and reducing the concentration of hydroxyl ions in solution.

It is well known that the hydroxyl ion concentration is primarily influenced by the dissolution of alkalis. It can be observed that the change in pH may be attributed to the alkali concentration in the pore solution. All of the paste samples with a pH below the control sample of 13.00 also had a reduction in total alkali concentration compared to the control. Conversely, the blends with an increase in pH displayed an increase in total alkalis, the exception again being the blend containing 35% FA2 with 10% metakaolin.

Figure 3-2 presents results for samples cured for 14 days at 80°C of the dissolution of potassium and sodium, respectively, with a focus on these systems; pastes containing binary blends of FA2, alumina oxide powder, or metakaolin and ternary blends of FA2 with alumina oxide powder or metakaolin. Solid lines represent the dissolution of potassium (K) and dashed lines represent the dissolution of sodium (Na).

Figure 3-2. Binder alumina content compared to alkali concentrations in pore solution for paste samples cured at 80°C for 14 days delineated by particular blend types. Solid lines represent K concentrations, dashed lines represent Na concentrations.



An increase in the alumina content was achieved by increasing the replacement of cement with SCM for each cementitious system shown in Figure 3-2. Each of the two data points connected by a line represents particular sets of SCMs at a low replacement and a high replacement. For example, the data points for FA2 represent a total

replacement of cement of 25% and 45% and the data points for FA2 at 20% Alumina represent a total replacements of 25% and 35%, as indicated previously in Table 3-5. For all of the samples, a higher replacement of cement resulted in a higher alumina content and lower concentration of potassium in solution.

It can be seen in Figure 3-2 that for all of the cementitious systems that an increase in the total alumina content within a blend resulted in a reduction of potassium available in solution. This is characterized by a downward trend in the concentration for all of the samples. Additionally, all of the blends containing SCMs resulted in a reduced potassium concentration when compared to the control blend.

From analysis of sodium dissolution in Figure 3-2, the control blend that contained no addition of aluminous materials displayed the lowest concentration of sodium in solution. A relationship between an increase in alumina content and a reduction in sodium concentration does not seem to exist from inspection of Figure 3-2. The largest concentration of sodium in solution occurred in the blend containing FA2 alone. This is most likely due to the high replacement level of FA2 providing an increased amount of available alkalis. As previously noted in Table 3-2, the amount of available alkalis in FA2 was considerably higher than the high alkali cement or the other fly ashes tested. This is particularly true for sodium where independent analysis determined that the available Na_2O of FA2 and the high alkali portland cement use in this study were 3.15 and 0.13%, respectively.

A major focus in ASR mitigation has been on reducing the total alkali concentration in solution. However, it may be determined that the mechanism behind the dissolution of potassium and sodium are not exactly the same. Recently, several studies have

indicated that the effect of potassium and sodium on silica and quartz dissolution is not identical^{23, 52-54} and a focus on the $\text{Na}_2\text{O}_{\text{eq}}$ may not be a reliable parameter when defining the potential of cements to cause ASR.⁵³ This is further supported by the results presented above.

The incorporation of alumina powder into a ternary blend with FA2, indicated by diamonds and squares Figure 3-2, did not seem to enhance the binding of sodium in hydration products (i.e. a reduction in pore solution concentration). When comparing a 25% total replacement of cement, represented by the left most point of the FA2, FA2 at 20% Alumina, and FA2 at 25%, any reduction in aqueous sodium as the alumina content is increased was most likely due to a slight reduction in the amount of fly ash used by the incorporation of alumina oxide powder. This may be referred to as a dilution effect. A similar observation cannot be made for the right most points because the total replacement of cement is 45% for the binary blend of FA2 and 35% for the ternary blends containing alumina oxide powder. However, the behavior does seem to exist when analyzing the right most points of the ternary blends with alumina oxide powder alone.

The paste samples containing ternary blends of FA2 with metakaolin showed an increase in sodium concentration. These ternary blends differ from the blends containing alumina oxide powder in that an increase in alumina is due to further replacement of cement with FA2 and not the alternative material, which is in this case metakaolin. An increase in sodium in solution is observed with a higher dosage of FA2. While the alumina content also increases, the overall increase in sodium is likely due to the higher total amount of alkali ($\text{Na}_2\text{O}_{\text{eq}}$) in the fly ash being released to the system.

The pastes containing binary blends of alumina oxide powder or metakaolin showed minimal amounts of available sodium in the pore solution compared to the control. Since these two manufactured products contain very small amounts of sodium (0.00% for alumina oxide powder and 0.09% for metakaolin), it is plausible that inconsequential amounts of sodium would be supplied to the pore solution. It should also be noted that the incorporation of these materials with a considerably high alumina content did not result in a reduction of the sodium content compared to the control. This may give rise to the suggestion that the mechanism in which alumina containing SCMs function to suppress expansion by ASR is primarily due to its ability to control aqueous potassium rather than sodium.

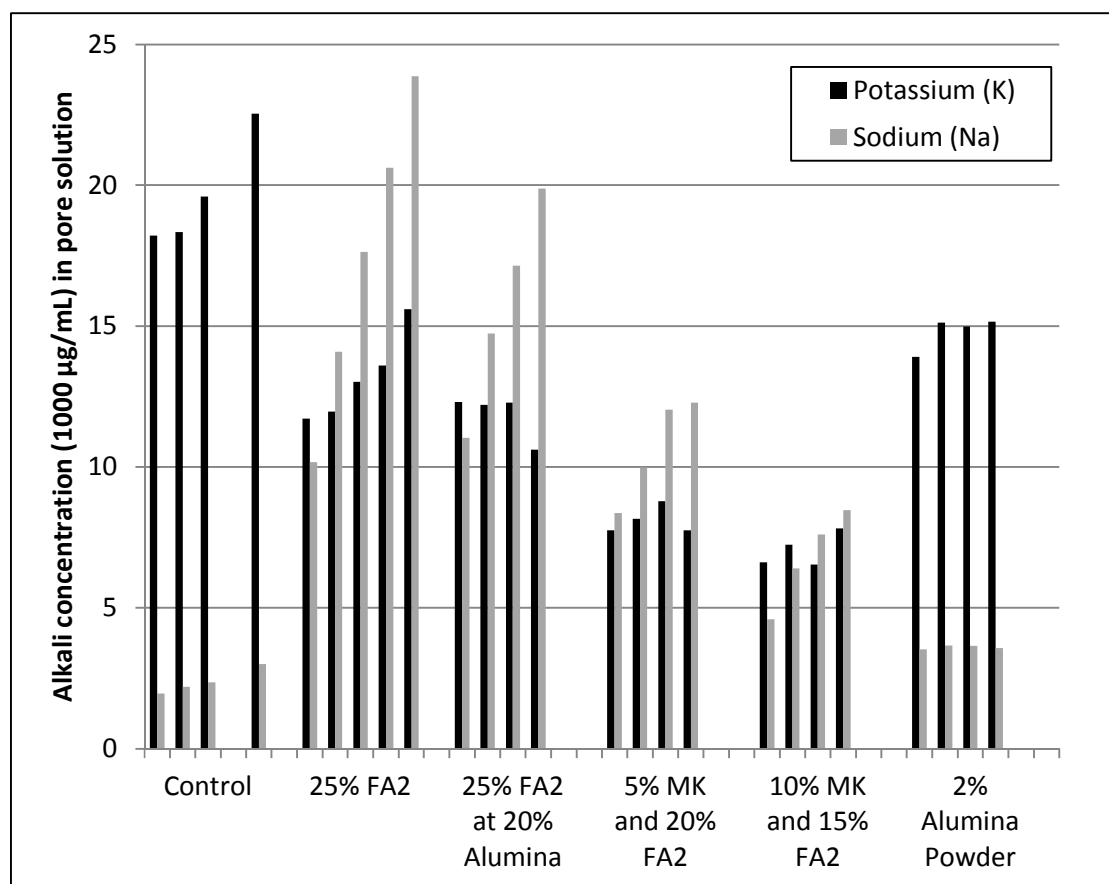
It remains unclear if the form of which alumina is contributed by diverse SCM materials plays a role in preventing the dissolution of or binding of alkalis from the pore solution, but a reduction in total alkalis seems to be influenced primarily by the reduction of potassium in solution as alumina content is increased.

When comparing aqueous alumina and potassium in Table 3-5, it appears that a considerable amount of alumina remains out of solution, below 10 $\mu\text{g/mL}$, when the concentration of potassium is above 6000-8000 $\mu\text{g/mL}$. It is not until the concentration of potassium is below 6000-8000 $\mu\text{g/mL}$ that a significant increase of alumina in solution occurs. A more specific range most likely does not exist due to the varying nature of each of the materials used; fly ash, alumina oxide powder, and metakaolin have different levels of reactivity, morphology, etc. The reduction in potassium coupled with the concentration of aqueous alumina remaining below 10 $\mu\text{g/mL}$, even though the alumina content of the blends is increasing, suggests that potassium is accompanying alumina as it is being used in the formation of supplementary hydration products. It is

believed that the increase of aqueous alumina once the potassium concentration is below 8000 $\mu\text{g/mL}$ is due to the system being flooded with an abundance of alumina or the system contains forms of alumina that do not participate in alkali binding. The concentration of aqueous potassium was below 8500 $\mu\text{g/mL}$ for all blends that contained a total alumina content above 10.00%. The three points with aqueous alumina greater than 10 $\mu\text{g/mL}$ also had some of the largest total aluminous contents (% Al_2O_3) with 10.23, 11.67, and 13.11%. These blends also contained greater than 40% FA2. There was no correlation between alumina content and sodium suggesting that potassium is preferred over sodium for alkali binding in cement systems containing alumina.

It has become clear that materials with elevated alumina contents can be utilized to improve the performance of a fly ash for the purpose of suppressing expansion due to ASR. To further support this, blends that had a total replacement of 25% were analyzed along with their resulting concentration of alkalis in their pore solution over the entire test period that included collection ages of 1, 7, 14, 28 and 90 days. Additionally, the binary blend of 2% alumina oxide powder was also shown to support the role of alumina. The paste samples cured at 80°C that had sufficient pore solution to be tested and their concentration of alkalis are displayed in Figure 3-3.

Figure 3-3. Alkali concentrations of pore solution for paste samples cured at 80°C for 1, 7, 14, 28, and 90 days.

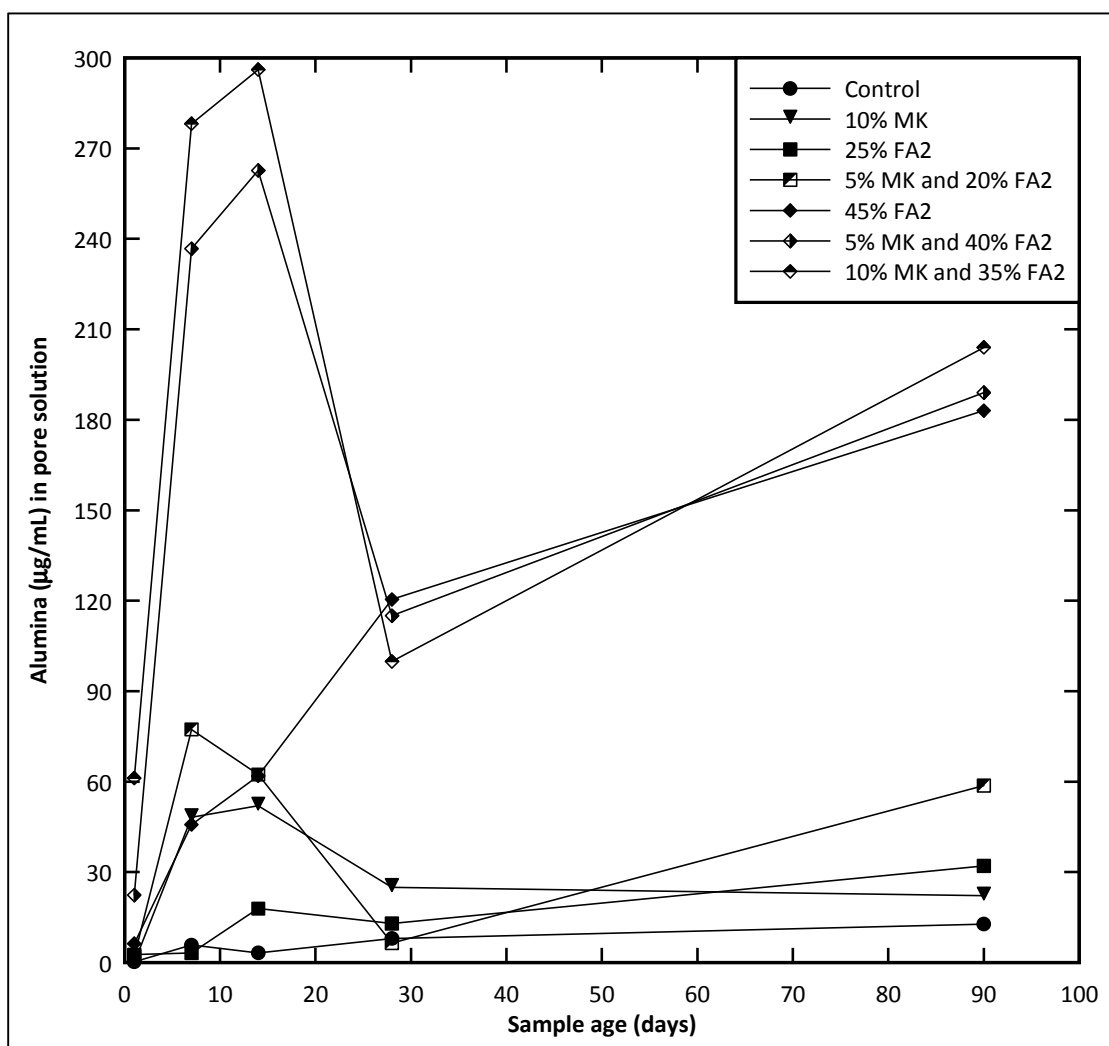


The control paste (portland cement only) shows aqueous alkali levels that correspond to the available potassium and sodium values presented in Table 3-1 (0.80 and 0.13 respectively). As expected, there is more aqueous potassium than sodium. When compared to the control paste in Figure 3-2, the incorporation of 25% FA2 fly ash results in a reduction of potassium and an increase in sodium in solution.

Aqueous potassium in the pore solution decreases with the incorporation of all SCMs compared to the control. This is similar to results previously discussed in Figure 3-2 that the binding of potassium may occur with incorporation of SCMs rich in alumina. The incorporation of alumina oxide powder to elevate the alumina content of FA2 to 20% reduced the dissolution of both potassium and sodium. It is key to note the dissolution rates, which can be expressed as the slope of the line created by the values for each sample. Set through the incorporation of alumina oxide powder, the dissolution rate of potassium for the blend containing FA2 at an elevated alumina content of 20% was greatly reduced, even displaying a negative trend from 14 to 28 days. The reduction in the dissolution rate of potassium can also be seen for blends containing FA2 with metakaolin. Additionally, the binary blend of 2% alumina oxide powder displayed a dissolution rate close to zero for the life of the sample. This blend also exhibited a reduction in potassium concentration and an increase in sodium concentration. The increase in sodium concentration may be due to its dissolution being required to keep charge balance within the solution while potassium is being bound into the cement matrix. For all samples containing FA2, the dissolution rate of sodium remains considerably unchanged and often greater than the control.

The question still remains if the form at which alumina is contributed by diverse SCM materials plays a role in preventing the dissolution of or binding of alkalis from the pore solution. An answer may be determined by monitoring the dissolution of alumina over time. Figure 3-4 displays the evolution of alumina concentration in the pore solution for select paste samples cured at 23C and tested at 1, 7, 14, 28, and 90 days.

Figure 3-4. Evolution of alumina concentration in pore solution of select paste samples containing FA2 and/or metakaolin and cured at 23C.



Once again analysis should start with the control blend, a paste containing only high alkali portland cement. For this blend, minimal amounts of alumina are present in the pore solution for the lifetime of the sample. The incorporation of 25% FA2 displayed a steady increase in the alumina concentrations for each of the sample ages tested. The

paste sample containing 10% metakaolin displays different behavior. Rather than an increase in alumina over time, alumina is rapidly dissolved into the pore solution and then removed for the creation of supplementary hydrates, most likely in the form of C-A-S-H.⁵¹ When 5% of FA2 was replaced by metakaolin to create a blend containing 5% metakaolin with 20% FA2, a new ternary evolution characteristic is observed. During the first week of hydration, the alumina concentration increases rapidly but then is greatly reduced until 28 days, similar to the blend containing only metakaolin. From 28 to 90 days, the alumina concentration rises slightly, similar to the blend containing 25% FA2. This evolution is even more noticeable for blends with a 45% total replacement of cement. Increasing the amount of FA2 to 45% greatly increased the alumina concentration over the entire sample age and reached 180 $\mu\text{g/mL}$ at 90 days. When 5% of FA2 was replaced with metakaolin, a rapid dissolution of alumina is displayed during the first two weeks of hydration followed by a rapid consumption up until 28 days. Again, this evolution of alumina concentration during the first two weeks of hydration is similar to the blend containing only metakaolin. From 28 days to 90 days, the alumina concentration is increased to similar values to the blend containing only FA2. Increasing the amount of metakaolin to 10% increases the alumina concentration during the first two weeks of hydration and the alumina concentrations also reach a value similar to the blend containing 45% FA2 at 90 days.

Figure 3-4 supports the idea that the alumina contained by metakaolin and fly ash may be considered similar, but not the same. The alumina contained by metakaolin dissolves more rapidly in high alkaline solutions at an earlier age and is therefore more readily available for ASR mitigation. Fly ash may contain alumina in forms other than Al[4] and would thus not participate in alkali binding through C-A-S-H development. Additionally,

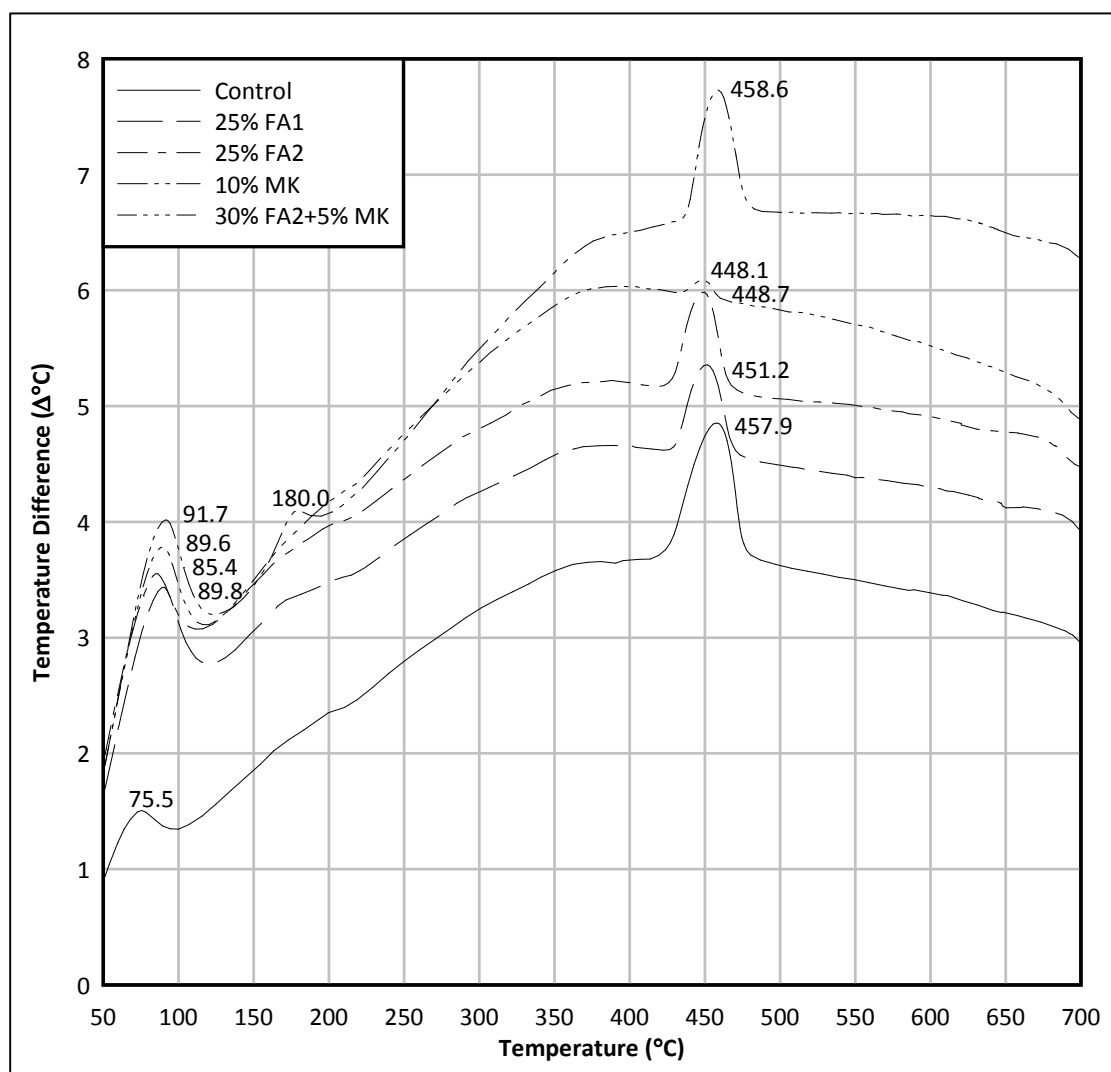
the quantity of alumina in an appropriate form may differ by fly ash and is dependent on the burning process that the fly ash was created, as previously mentioned.

3.3.3 Thermal Analysis

Thermal analysis was performed to determine the mechanism of alumina in reducing ASR related expansion by examining the difference in hydration products formed. This included select testing using Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) on a total of 5 samples to determine the composition of pastes with high alkali cement supplemented with FA1, FA2 or metakaolin as well as a ternary blend of FA2 with metakaolin.

Figure 3-5 displays the DTA results collected for binary blends containing 25% FA1, 25% FA2, or 10% metakaolin as well as a ternary blend of 30% FA2 with 5% metakaolin.

Figure 3-5. DTA curves from 50 to 700°C at 10°C/min for samples cured at 80°C for 28 days.

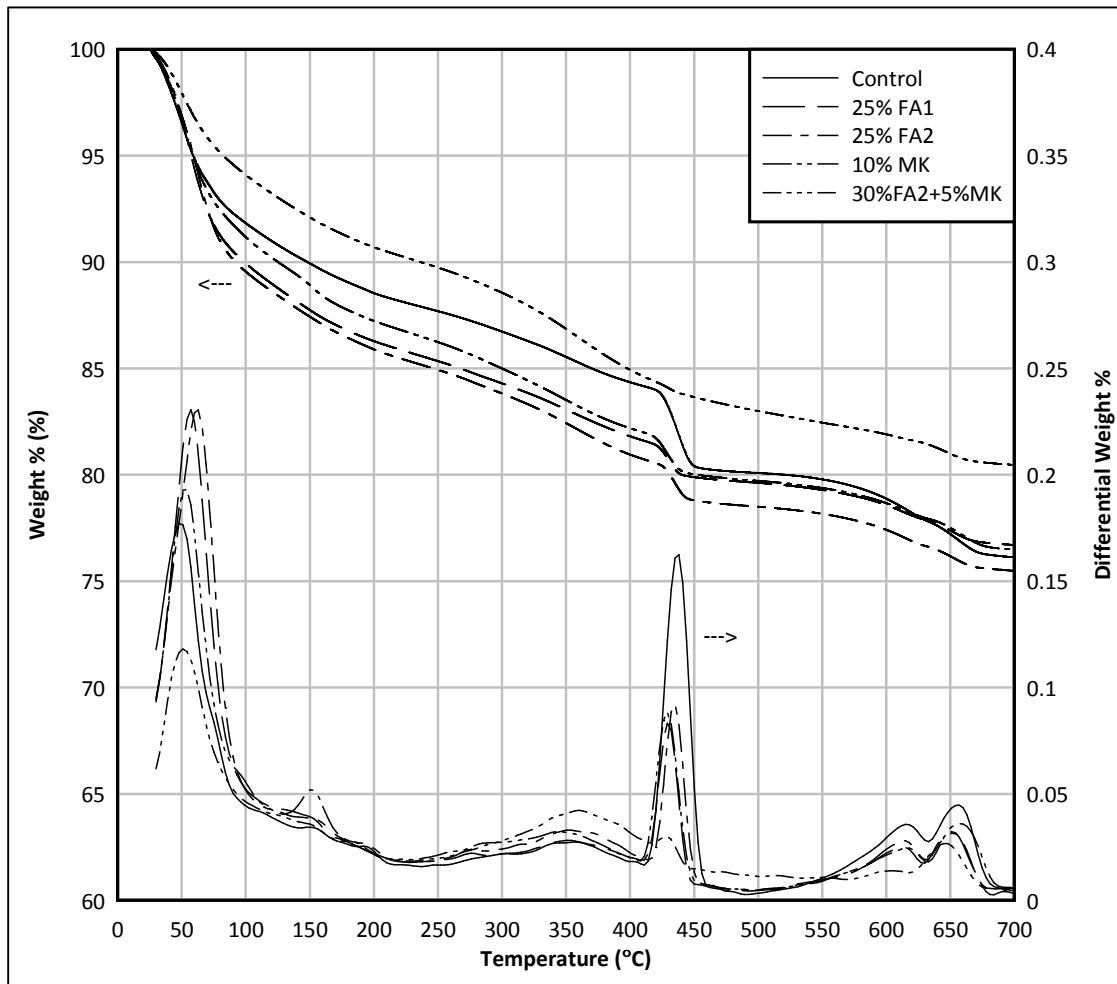


The DTA results display a loss of unbound water in the 50-120°C range followed by a peak from 425-475°C due to a phase change of the $\text{Ca}(\text{OH})_2$ present in the blends. It can be seen that the ternary blend contained minimal $\text{Ca}(\text{OH})_2$, as seen by a diminished

response at the latter temperature spike. Additionally, the blend containing 10% metakaolin exhibited a response at 180°C that may be attributed to an alteration in the C-S-H incorporating alumina or the development of other alumina containing hydrates (stratlingite, hydrogarnet, C_2AH_6 , C_2AH_8 , C_4AH_{13}).⁵⁵

Figure 3-6 displays the TGA results, loss of mass and corresponding derivative curves presented as differential mass, for the same samples analyzed by DTA.

Figure 3-6. TGA curves from 26 to 700°C at 10°C/min for samples cured at 80°C for 28 days.



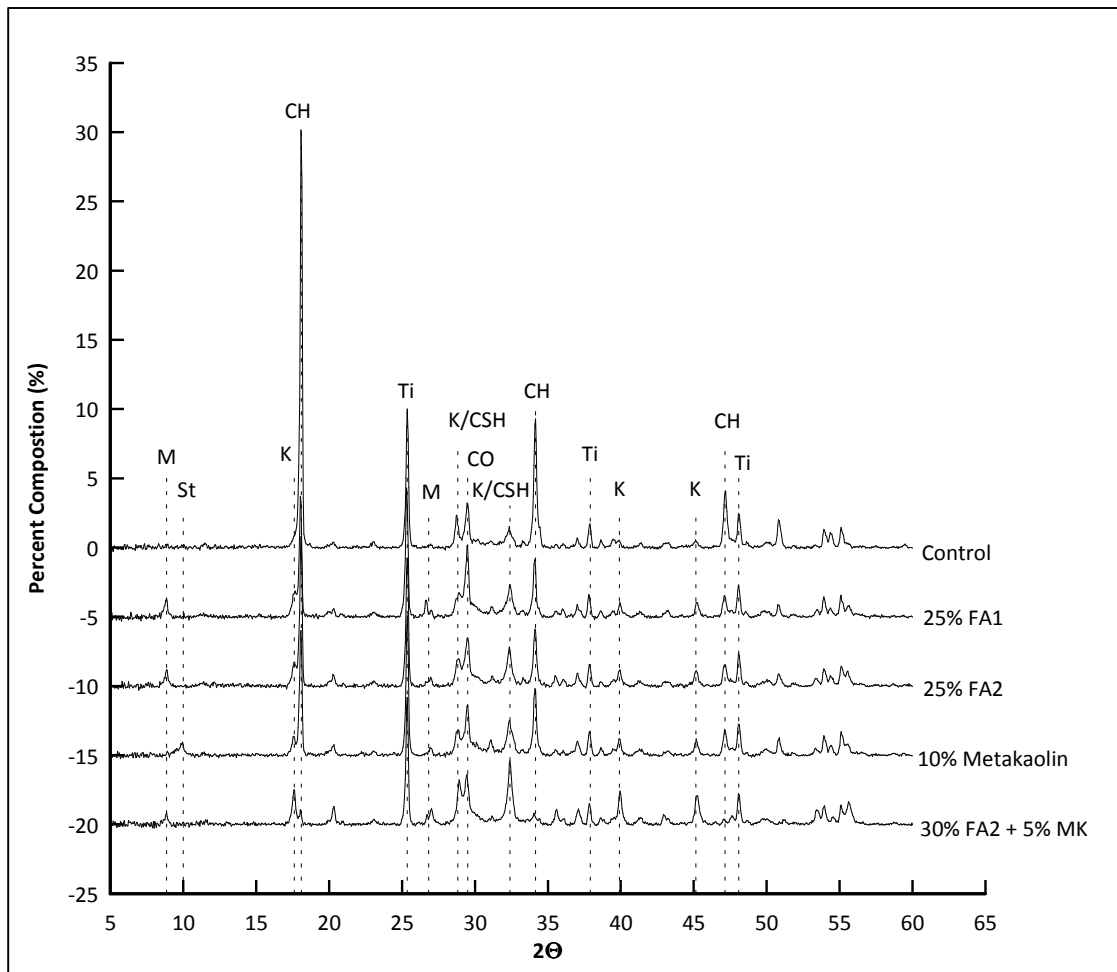
TGA results show loss of mass until 100°C due to the release of unbound water followed by a rapid loss between 425-475°C due to the presence of Ca(OH)_2 , similar to DTA. The blend containing 10% metakaolin displayed a minimal loss of mass at the latter temperatures, confirming the DTA results and structure of the material that the blend is capable of consuming the Ca(OH)_2 created by the hydration of cement through

pozzolanic reaction. This can also be seen by the derivative curves displayed below the TGA curves in Figure 3-6 where the curve is minimal for the blend containing 10% metakaolin when compared to the control. For all of the blends containing fly ash, the magnitude of the change in mass on the TGA curves and the magnitude of the derivative curves are lessened in the 425-475°C temperature range. A response at 150°C, seen primarily in its derivative curve, for the blend containing 10% metakaolin supports the idea of an alteration in the calcium silicate hydrates as seen in the DTA results.⁵⁵

3.3.4 X-Ray Diffraction

X-ray diffraction results provide a semi-quantitative analysis of the crystalline structures present in the blends tested. The values presented from the incorporation of titanium oxide provide a reference in establishing an estimate on the amount of particular structures. The values obtained for the standard were unchanged for each sample type and therefore allowed the results to be normalized against the peak intensity for each blend. Figure 3-7 displays the normalized results for X-ray diffraction of the five blends tested.

Figure 3-7. XRD patterns of pastes. (M) Muscovite, (St) Stilbite, (K) Katoite, (CH) Calcium Hydroxide, (Ti) Titanium Oxide, (CSH) Calcium Silicate Hydroxide, and (CO) Calcium Carbonate.



As previously discussed, the elimination of reactive silica can eliminate expansion due to ASR. This can be achieved by lowering the pH of the pore solution through the binding of alkalis or reducing the amount of $\text{Ca}(\text{OH})_2$. It can be seen by inspection of the peak intensity at 18.00° that $\text{Ca}(\text{OH})_2$ comprised approximately 30% of the control blend.

Through similar inspection, the blends containing FA1, FA2 or metakaolin display a reduction in Ca(OH)_2 to 8.70, 10.77, and 9.02% respectively. The ternary blend of 30% FA2 and 5% metakaolin reduced the amount of Ca(OH)_2 to 0.82%, nearly consuming all of the portlandite produced by the hydration of portland cement. The results obtained by XRD show that the pozzolanic nature of the fly ash and metakaolin result in considerable reduction of Ca(OH)_2 and that efficacy is further improved by the use of a ternary blend.

The consumption of Ca(OH)_2 by pozzolanic activity resulted in the formation of Katoite, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$. When $x=3$, the species is also known as tricalcium aluminate hydrate (C_3AH_6) in hydrated cement. None of the blends contained ettringite, $\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$, which would be designated by responses at 9.06° and 15.73° . The lack of ettringite indicates that the alumina contributed by the SCM materials does not produce ettringite phases but rather favors the formation other hydrates that could possibly bind alkalis.

While X-ray diffraction identifies the presence of crystal structures capable of binding K^+ and Na^+ ions from the pore solution, it does not identify amorphous materials that could also possess similar capabilities. Because C-S-H gel is almost amorphous, X-ray diffraction gives only very general indications of its nanostructure. The reactions between aqueous calcium and silicate ions normally produce products with intermediate crystallinity.³⁶ The alteration of such structures into a C-A-S-H product would yield a similarly intermediate crystalline structure. As a result, other analytical techniques should be investigated, such as MAS NMR, to characterize calcium aluminate phases in fly ash and metakaolin cement systems.

For the materials tested, X-ray diffraction did detect the formation of potentially alkali binding crystal structures. Through analysis of the responses in the 8.00° to 10.00° range, it was determined that Muscovite of the mica family, $KAl_2(Si_3Al)O_{10}(OH)_2$ (in blends with fly ash) and zeolitic Stilbite, $NaCa_4(Si_{27}Al_9)O_{72} \cdot 28(H_2O)$ or $Na_9(Si_{27}Al_9)O_{72} \cdot 28(H_2O)$ in the sample with 10% metakaolin had formed. The formation of such structures indicates that the incorporation of alumina into a blend through cement supplementation with SCM materials does result in the binding of alkalis.

Muscovite is a complex hydrous potassium-aluminum silicate mineral. The structure of muscovite is layered aluminum silicate sheets weakly bonded together by layers of potassium ions.

Stilbite, which requires relatively high activity of water for stability, differs from other related zeolites. A large cage formed by the silica aluminum framework is occupied by calcium ions surrounded by water molecules. Sodium ions are attached to one or two water molecules as well as framework oxygens.⁵⁶

3.4 CONCLUSION

In an effort to better determine the mechanism that which alumina contributes to reducing expansion due to ASR, several different procedures were performed. The first involved the ASTM C1567 Accelerated Mortar Bar Test (AMBT) for mortar samples containing fly ashes of various constituent levels as well as augmented fly ash with elevated alumina content through the incorporation of alumina oxide powder. AMBT samples were also tested for blends incorporating binary and ternary blends of ultra-fine fly ash and metakaolin, materials considered to have elevated alumina contents when compared to the previously augmented fly ashes. Part two of this research

related the pore solution chemistry of the cementitious systems tested in part one to their expansions. DTA, TGA, and XRD analysis concluded the investigation in an attempt to determine if alkali binding structures were being developed through the incorporation of materials containing significant amounts of alumina. The following conclusions were derived:

- Fly ash can reduce expansion due to ASR provided the appropriate replacement level is used.
- Fly ashes with alumina contents greater than 20% are more effective in controlling ASR than those with levels less than 20%.
- An alumino-siliceous content (Al+Si) greater than 36.50% for cementitious systems incorporating fly ash may be required to suppress expansion due to ASR.
- Ultra-fine fly ash is more effective than normal fineness fly ash in controlling ASR at lower replacement levels. Metakaolin is more effective in controlling ASR than ultra-fine fly ash at lower replacement levels. An increase in alumina content corresponds to an increase in effectiveness in controlling expansion due to ASR at lower replacement levels.
- Ternary blends containing materials with increased alumina contents are more efficacious in controlling ASR at overall lower replacement levels when compared to binary blends of fly ash alone.
- The use of fly ash may result in higher alkali contents and pH in the pore solution of hardened cement systems. The inclusion of products containing alumina in a ternary blend, such as metakaolin, can reduce this effect.
- DTA, TGA, and XRD demonstrate that Ca(OH)_2 is reduced through pozzolanic action for blends containing SCM materials and that a synergistic effect exists for

ternary blends of fly ash and metakaolin; nearly all of the Ca(OH)_2 was depleted for a ternary blend of 30% FA2 and 5% metakaolin.

- XRD results support the development of crystal structures that require alumina and alkalis for formation, supporting the idea that the inclusion of alumina into cementitious systems results in the binding of alkalis from the pore solution in such structures.
- Alterations to C-S-H/C-A-S-H are seen in DTA, TGA, and XRD. However, further work using NMR or other appropriate methods is mentioned to determine exact structural alterations.

While fly ashes can be characterized by their chemical constituents, these components may be bound and react differently from one fly ash to another, which is anticipated to have a significant effect on the ability of a given fly ash to control ASR. Despite contributing a predetermined amount of alumina, determined by oxide analysis, the form in which alumina is contributed by an SCM can vary. Thus, the effectiveness of an SCM containing alumina in mitigating ASR can vary as well. Morphological properties may also have a direct influence on the availability at which the alumina provided is capable of participating in mitigation, i.e. the percentage of alumina contributed by a fly ash that influences the suppression of expansion due to ASR may have considerable variation. Thus, research into the mineralogical organization and structure of the alumina contained by fly ash would enhance the understanding of how alumina can be used to improve the efficacy of fly ash systems to mitigate alkali-silica reaction.

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4 GENERAL CONCLUSION

Strategies to mitigate alkali-silica reaction, one of the leading causes of concrete deterioration, have been researched since the 1940s. The replacement of fly ash for a fraction of portland cement has proven to be an effective method in decreasing ASR expansion. However, the type and amount of fly ash to be recycled for use in concrete has been limited by many challenges. This includes the contribution of alkalis from the fly ash, which may exacerbate ASR and hinder the effectiveness of the fly ash.

The goal of this research project, therefore, was to evaluate the ability for alumina contained by fly ash, or other supplementary cementitious materials (SCM) materials, to counter the contribution of alkalis from fly ash and to potentially provide improved ASR mitigation. Testing to determine such mechanisms included: accelerated mortar bar testing to assess the effectiveness of different SCM materials with varying alumina contents to control ASR expansion; pore solution analysis of paste samples to determine how the contribution of alkalis was influenced by the inclusion of alumina into a cementitious system; thermal analysis to monitor the pozzolanic reactivity of SCM materials with varying alumina contents; and X-ray diffraction analysis to investigate the ability for SCM materials containing alumina to generate alkali binding crystalline structures.

Two manuscripts have been assembled and were included in this thesis. The first, entitled *Alkali-Silica Reactivity and the Role of Alumina* discussed the potential mechanism by which alumina may be responsible for the binding of alkalis when introduced into a cementitious system through limited SCM materials. The second manuscript, *The Efficacy of High Alumina SCMs to Control ASR*, presents the results from accelerated mortar bar testing as well as results from pore solution extraction and

analysis, thermal analysis, and X-ray diffraction on cement-SCM paste samples. It was concluded that fly ashes with higher amounts of alumina had the potential to bind potassium from solution as well as generate crystalline structures with potassium and sodium binding potential. The comparison between accelerated mortar bar testing and pore solution analysis established that the form of alumina contributed by a SCM material may vary, especially in terms of its efficacy in reducing ASR. Additionally, the alumina contributed by metakaolin may be useful in improving the efficacy of a particular fly ash through the implementation of a ternary blend. Based on this work and work by others, the coordination of alumina in hydrates may play a role in its ability to participate in the formation of hydrate structures and as a result play a profound role in ASR mitigation.

The following conclusions were derived through the research conducted in this investigation:

- Fly ash can reduce expansion due to ASR provided the appropriate replacement level is used.
- Results showed that alumina contributed from alumina oxide powder when replacing a portion of cement correlates to lower expansion. Also, an alumina content of 20% or higher is recommended when fly ash is used to mitigate ASR expansion based on the results of this study.
- An alumino-siliceous content (Al + Si) greater than 36.50% for cementitious systems incorporating fly ash and alumina oxide powder may be required to suppress expansion due to ASR.
- The three types of ternary blends investigated show that higher alumina content improved mitigation of ASR expansion when high-alkali portland cement was

combined with fly ash and one of the following: alumina powder, metakaolin, or ultra-fine fly ash.

- Ultra-fine fly ash is more effective than normal fineness fly ash in controlling ASR at lower replacement levels. Metakaolin is more effective in controlling ASR than ultra-fine fly ash at lower replacement levels. An increase in alumina content corresponds to an increase in effectiveness in controlling expansion due to ASR at lower replacement levels.
- Metakaolin displayed an increased ability to suppress ASR expansion due to its primarily alumino-siliceous composition. Lower levels of metakaolin were needed to control expansion below 0.10% (AMBT limit) in this study when compared to the amount of fly ash required to achieve the same result.
- Artificially increasing the alumina content of a fly ash through the incorporation of alumina oxide powder, metakaolin, or ultra-fine fly ash improved the effectiveness of certain fly ashes in this study to mitigate ASR expansion.
- The use of fly ashes with high sodium oxide equivalent may result in higher alkali contents and pH in the pore solution of hardened cement systems. The inclusion of products containing alumina in a ternary blend, such as metakaolin, can reduce this effect.
- DTA, TGA, and XRD demonstrate that Ca(OH)_2 is reduced through pozzolanic action for blends containing SCM materials and that a synergistic effect exists for ternary blends of fly ash and metakaolin; nearly all of the Ca(OH)_2 was depleted for a ternary blend of 30% FA2 and 5% metakaolin.
- XRD results support the development of crystal structures that require alumina and alkalis for formation, supporting the idea that the inclusion of alumina into

cementitious systems results in the binding of alkalis from the pore solution in such structures.

- Alterations to C-S-H/C-A-S-H are seen in DTA, TGA, and XRD. However, further work using NMR or other appropriate methods is mentioned to determine exact structural alterations.

Further analysis may be required to investigate binding characteristics of alkalis in cement-fly ash systems that contain considerable amounts of alumina into hydration products. MAS-NMR on cement-fly ash paste samples containing various amounts of alumina may prove to be a powerful technique for the characterization of hydrates containing alumina. Additionally, testing to correlate the presented results with results from ASTM C1293 (concrete prism test), chinese accelerated mortar bar test (CMBT), outdoor exposure blocks, and field structures containing SCMs with high alumina contents is warranted. Such correlations would identify if the expansion limits provided by ASTM C1260 and ASTM C1567 are valid for concrete incorporating SCM materials with elevated alumina contents to withstand deleterious ASR. While this study was able to present a significant amount of new information indicating a potential role for alumina in the mitigation of deleterious ASR, further investigation is suggested for to fully elucidate mechanisms and to provide recommendations for systems able to resist deleterious ASR.

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APPENDIX A

APPENDIX A

This appendix presents additional testing data that contributed to the results in Manuscript 1, but was not directly included in the manuscript.

Figure A-1: Alumina content from all cementitious materials and resulting pore solution pH and total alkali contents (Na + K) for pastes samples cured at 80°C for 14 days.

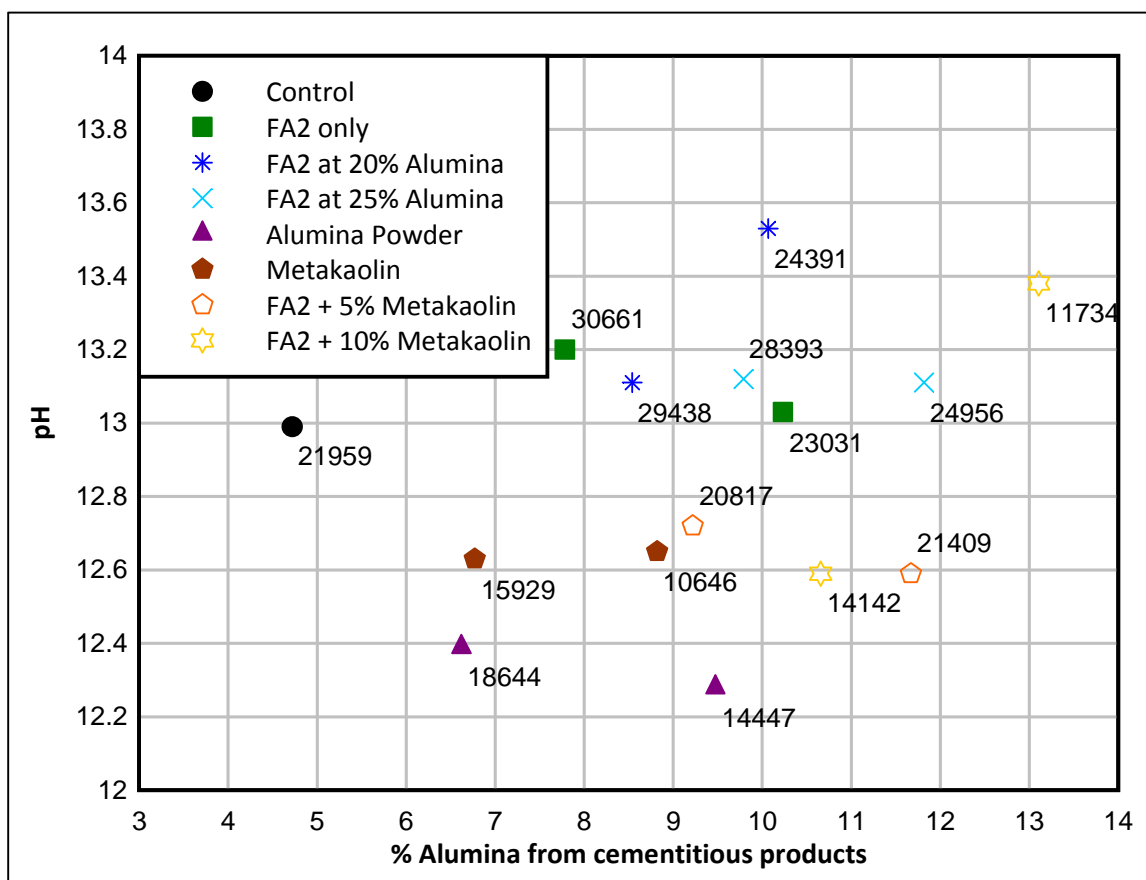


Table A-1: Pore solution alkali contents for paste samples cured at 80°C that had sufficient pore solution to be tested.

	Temp (°C)	Cure Time	Al ₂ O ₃ input	Pore Solution Concentrations				
				Al (ug/mL)	Ca (ug/mL)	Si (ug/mL)	K (ug/mL)	Na (ug/mL)
Control	23	1	4.72	42.3	48	18.0	19,733	1,933
		1b	4.72	0.5	81	18.9	23,056	3,102
		7	4.72	5.8	362	60.5	21,331	2,052
		14	4.72	3.2	92.3	21.9	22,155	2,123
		28	4.72					
		90	4.72	13	207	40.4	23,889	2,482
	80	1	4.72	0.25	85	8.1	18,213	1,961
		7	4.72	3.64	256	17.7	18,339	2,198
		14	4.72	6.33	271	27.2	19,595	2,364
		14b	4.72	3.76	181	19.4	16,828	1,980
		28	4.72					
		90	4.72	0.8	130	14	22,550	3,000
25% FA2	23	1	7.7825	2.61	41	15.9	15,067	6,273
		7	7.7825	3.21	34	13.8	15,692	8,500
		14	7.7825	17.9	167	62.3	15,967	9,887
		28	7.7825	13.0	48	30.4	15,902	11,630
		90	7.7825	32	196	80.1	26,627	16,539
	80	1	7.7825	5.59	61	17.8	11,716	10,171
		7	7.7825	23.0	230	64.9	11,965	14,085
		14	7.7825	0.0	60.8	9.0	13,024	17,637
		28	7.7825	1.41	80	12.8	13,608	20,629
		90	7.7825	6.14	112	26.1	15,603	23,872

Continued

45% FA2	23	1	10.2325	6.31	23	20.8	11,893	9,818
		7	10.2325	46	12.0	36.4	11,900	14,163
		14	10.2325	62	16	46.0	10,666	14,494
		28	10.2325	120	14	59.1	10,313	15,796
		90	10.2325	183	161	160.0	11,909	21,691
	80	1	10.2325	38	13	31.8	8,253	14,160
		7	10.2325	83	59	78.8	7,396	15,254
		14	10.2325	54	75	101.0	7,149	15,881
		28	10.2325	47	27	104.1	8,965	21,235
		90	10.2325	24.8	35.1	78.4	11,044	30,685
25% FA2 at 20% Alumina	23	1	8.54					
		7	8.54	4.83	42	16.2	14,620	7,959
		14	8.54	4.17	38.4	23.9	11,974	12,103
		28	8.54	9.27	77.9	38.3	12,393	14,223
		90	8.54	3.93	33.6	19.7	14,571	14,840
	80	1	8.54	4.31	47	13.3	12,306	11,026
		7	8.54	7.02	85	48.0	12,208	14,733
		14	8.54	0.13	24.1	3.7	12,284	17,154
		28	8.54	0.66	59.8	14	10,615	19,881
		90	8.54					
35% FA2 at 20% Alumina	23	1	10.068	4.36	50	15.0	13,324	7,884
		7	10.068	4.8	22.0	20.6	13,218	10,853
		14	10.068	8.49	37.5	26	10,371	14,162
		28	10.068	44.8	23	41.2	13,217	14,584
		90	10.068	17.5	15.8	52	11,521	17,541
	80	1	10.068	3.66	45	17.7	7,577	13,347
		7	10.068	1.2	64.3	17.3	7,311	15,427
		14	10.068	8.54	16.6	29.1	7,234	17,157
		28	10.068	2.08	43.3	23.6	8,326	20,123
		90	10.068	7.71	33.1	36.8	7,569	17,427

Continued

25% FA2 at 25% Alumina	23	1	9.79	3.02	52	25.2	15,993	6,279
		7	9.79	3.89	45	16.8	15,426	8,008
		14	9.79	32	367	100	13,025	11,687
		28	9.79	115	1122	169	14,516	11,321
		90	9.79	8.59	67.9	34.5	13,694	13,267
	80	1	9.79	3.78	48	12.6	12,113	10,672
		7	9.79	3.8	63.6	16.9	11,504	14,366
		14	9.79	3.39	82	18.3	12,545	15,848
		28	9.79	11.4	160	29.6	13,205	19,603
		90	9.79					
35% FA2 at 25% Alumina	23	1	11.818	1.76	49	7.9	12,757	6,723
		7	11.818	6.60	33	12.8	13,049	9,268
		14	11.818	28	30.8	60.8	11,570	14,064
		28	11.818	12.6	34	70.9	13,326	13,275
		90	11.818					
	80	1	11.818	11.6	23.1	36.8	12,041	16,525
		7	11.818	7.12	17.6	27.3	7,116	14,859
		14	11.818	1.1	58.6	24.0	8,345	16,611
		28	11.818	1.05	59.3	10.4	7,825	18,122
		90	11.818					
5% Metakaolin	23	1	6.7695	1.89	84	8.9	16,477	3,135
		7	6.7695	13.9	46	19.0	13,166	2,781
		14	6.7695	2.9	60.7	15.4	10,788	2,617
		28	6.7695	4.28	49.7	13.7	11,085	2,795
		90	6.7695	3.63	49.2	14.4	11,559	2,981
	80	1	6.7695	4.13	154	13.9	12,328	3,130
		7	6.7695	0.68	99.5	7.6	12,792	3,540
		14	6.7695	7.50	169	17.8	12,631	3,297
		28	6.7695	2.47	169	12.3	12,246	3,463
		90	6.7695					

Continued

20% FA2 and 5% Metakaolin	23	1	9.2195	2.01	67	6.8	11,489	5,929
		7	9.2195	77.3	126	55.3	8,476	6,127
		14	9.2195	62.4	54	47.8	8,224	6,481
		28	9.2195	6.5	31.7	22.4	9,282	8,339
		90	9.2195	58.7	10.6	46.1	7,912	8,889
	80	1	9.2195	125	1117	236	7,752	8,361
		7	9.2195	12.1	36	21.2	8,165	9,980
		14	9.2195	2.0	45.9	11.9	8,781	12,036
		28	9.2195	1.19	45.8	10.7	7,755	12,280
		90	9.2195					
40% FA2 and 5% Metakaolin	23	1	11.6695	22	19.4	23.4	8,774	10,226
		7	11.6695	237	10	41.3	5,638	8,292
		14	11.6695	263	7	44.1	5,879	9,443
		28	11.6695	115	13.6	30.4	5854	10524
		90	11.6695	189	7	66.5	5,412	11,637
	80	1	11.6695	167	33	49.3	5,118	9,324
		7	11.6695					
		14	11.6695	99	26	72.3	5,939	15,470
		28	11.6695	63	12	72.9	5,215	16,551
		90	11.6695					
10% Metakolin	23	1	8.819					
		7	8.819	48.2	18	17.3	8,549	2,132
		14	8.819	52.0	28	18.2	7,976	1,991
		28	8.819	51	21.0	23.4	9,486	2,378
		28b	8.819	28	28.5	12.8	7,790	2,249
		90	8.819	22.2	26.9	14.4	8,175	2,370
	80	1	8.819	1.49	62.7	10.6	8,281	2,365
		7	8.819	1.14	117	7.9	9,670	2,948
		14	8.819	1.49	62.7		8,281	2,365
		28	8.819					
		90	8.819					

Continued

15% FA2 and 10% Metakaolin	23	1	10.6565	14.4	26	23.7	10,001	4,762
		7	10.6565	85	11.1	25.2	6,112	4,390
		14	10.6565	130	8	28.0	6,279	4,352
		28	10.6565	119	52.6	35.3	6,901	4,651
		90	10.6565	72.9	18.5	55.9	5,954	4,863
	80	1	10.6565	19.1	82	26.8	6,618	4,593
		7	10.6565	13.9	32	19.9	7,243	6,395
		7b	10.6565	66.0	471	131.0	7,403	6,608
		14	10.6565	6.22	34.5	15.4	6,538	7,604
		28	10.6565	11.9	148	34.4	7,826	8,467
		90	10.6565					
35% FA2 and 10% Metakaolin	23	1	13.1065	61	16	34.5	6,559	7,196
		7	13.1065	278	6	34.6	4,455	6,310
		14	13.1065	296	35	77.0	4,131	6,407
		28	13.1065	100	84.9	96.5	6,209	11,268
		90	13.1065	204	15	47.5	3,733	7,058
	80	1	13.1065	136	12	39.1	3,804	5,633
		7	13.1065					
		14	13.1065	102	11.7	40.1	3,450	8,284
		28	13.1065					
		90	13.1065					
2% Alumina Oxide Powder	23	1	6.6216	1.60	65	6.7	15,485	2,967
		7	6.6216	2	85	12.3	15,374	3,288
		14	6.6216	3.6	97.5	18.3	17,752	3,350
		28	6.6216	1.64	73.9	11.2	15,789	3,342
		90	6.6216	1.44	60.6	8.7	16,491	3,571
	80	1	6.6216	0	47	12.8	13,904	3,531
		7	6.6216	0.21	172	3.4	15,130	3,664
		14	6.6216	0.05	105	4.4	14,992	3,652
		28	6.6216	0.02	124	2.9	15,159	3,580
		90	6.6216					

Continued

5% Alumina Oxide Powder	23	1	9.474	1	74	28.1	13,577	2,783
		7	9.474	1	73	6.8	14,753	3,224
		14	9.474	1	64	7.0	14,452	3,227
		28	9.474					
		90	9.474	0.95	68.1	12	15,749	3,683
	80	1	9.474	0.63	162	12.4	13,680	3,212
		7	9.474	0.69	187	4.6	15,514	3,607
		7b	9.474	0.02	206	2.8	13,531	3,231
		14	9.474	0.0	24.0	3.7	11,844	2,604
		28	9.474	2.4	184	12.7	17,720	4,077
		90	9.474					