AN ABSTRACT OF THE THESIS OF

Kelsea Schwing for the degree of Master of Science in Civil Engineering presented on November 12, 2010.

Title: Use of Fly Ash in the Mitigation of Alkali-Silica Reaction in Concrete

Abstract approved:

_____

Jason H. Ideker

Alkali-silica reaction (ASR) is one of the leading causes of concrete deterioration throughout the world, and affects both structural and non-structural elements. Despite strong research efforts since its discovery by Stanton in the late 1930s, this deteriorating reaction is still not clearly understood nor are proper preventative measures effectively applied to reduce the risk of ASR. Central to the debate is a lack of clear understanding about how supplementary cementing materials (SCMs), in particular fly ash, limit the progression of the reaction. One reason for avoiding the use of a certain fly ash in concrete is the alkali content of the particular fly ash. Because there is very little guidance and no standardized test to accurately measure the contribution of alkalies from a given ash in a real concrete mixture, many ashes are simply avoided. Development and standardization of a rapid test method to accurately predict the contribution of fly ash alkalies to the pore solution of concrete is the goal of a multi-phase project in the Civil Engineering department at Oregon State University. The first phase of the project included performing a series of ASTM C 1567 tests (Standard Test Method for Potential Reactivity of Aggregates (Mortar-Bar Method)) utilizing various materials and replacement levels to determine the effectiveness of different fly ashes in the mitigation of ASR expansion. Also, predictive equations introduced by Malvar et al were applied to a variety of materials to determine the efficacy of different fly ashes to control alkali silica reaction based on chemical composition. In addition, pore solution evaluation was

Report Documentation Page		*Form Approved* *OMB No. 0704-0188*

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE **NOV 2010**	2. REPORT TYPE	3. DATES COVERED **00-00-2010 to 00-00-2010**
4. TITLE AND SUBTITLE **Use of Fly Ash in the Mitigation of Alkali-Silica Reaction in Concrete**		5a. CONTRACT NUMBER
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		5d. PROJECT NUMBER
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Oregon State University,Civil Engineering,Corvallis,OR,97331**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Alkali-silica reaction (ASR) is one of the leading causes of concrete deterioration throughout the world, and affects both structural and non-structural elements. Despite strong research efforts since its discovery by Stanton in the late 1930s, this deteriorating reaction is still not clearly understood nor are proper preventative measures effectively applied to reduce the risk of ASR. Central to the debate is a lack of clear understanding about how supplementary cementing materials (SCMs), in particular fly ash, limit the progression of the reaction. One reason for avoiding the use of a certain fly ash in concrete is the alkali content of the particular fly ash. Because there is very little guidance and no standardized test to accurately measure the contribution of alkalies from a given ash in a real concrete mixture, many ashes are simply avoided. Development and standardization of a rapid test method to accurately predict the contribution of fly ash alkalies to the pore solution of concrete is the goal of a multi-phase project in the Civil Engineering department at Oregon State University. The first phase of the project included performing a series of ASTM C 1567 tests (Standard Test Method for Potential Reactivity of Aggregates (Mortar-Bar Method)) utilizing various materials and replacement levels to determine the effectiveness of different fly ashes in the mitigation of ASR expansion. Also, predictive equations introduced by Malvar et al were applied to a variety of materials to determine the efficacy of different fly ashes to control alkali silica reaction based on chemical composition. In addition, pore solution evaluation was conducted using a specialized extraction device, one of only 3 of its kind in the United States. This process, carried out on 265 paste samples made of various combinations of cements, fly ashes and fly ash replacement levels, enabled the authors to evaluate the effects of curing temperature, time and raw material chemistry on the paste pore solution. The results of the pore solution analysis were compared against the expansion tests and it was concluded that aluminum also plays a key role in the ability of a given ash to mitigate alkali-silica reaction.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**128**	

conducted using a specialized extraction device, one of only 3 of its kind in the United States. This process, carried out on 265 paste samples made of various combinations of cements, fly ashes and fly ash replacement levels, enabled the authors to evaluate the effects of curing temperature, time and raw material chemistry on the paste pore solution. The results of the pore solution analysis were compared against the expansion tests and it was concluded that aluminum also plays a key role in the ability of a given ash to mitigate alkali-silica reaction.

Use of Fly Ash in the Mitigation of Alkali-Silica Reaction in Concrete

by
Kelsea Schwing

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Presented November 12, 2010
Commencement June 2011

Master of Science thesis of <u>Kelsea Schwing</u> presented on <u>November 12, 2010</u>.

APPROVED:

_____

Major Professor, representing Civil Engineering

_____

Head of the School of Civil and Construction Engineering

_____

Dean of the Graduate School

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.

_____

Kelsea Schwing, Author

ACKNOWLEDGEMENTS

First and foremost, I want sincerely thank my advisor and mentor Dr. Jason H. Ideker. His dedication, assistance and patience with me over the years is truly appreciated.

Dr. Kevin J. Folliard and Dr. Michael D.A. Thomas also helped me tremendously through this process and I am grateful to them.

I also want to thank all my colleagues and friends that have supported me along the way. Your companionship will never be forgotten!

Dr. Todd Scholz, Dr. Skip Rochefort and Roger Graham served on my thesis committee and their questions and comments are appreciated.

Finally, I want thank my parents and sister who supported me endlessly through my many years of education and my loving husband Thomas, who not only assisted me, but also put up with all of my complaining and grumbling. Thank you for your love and support!

CONTRIBUTION OF AUTHORS

Dr. Jason H. Ideker advised on data collection, analysis and interpretation of Chapters 2, and 3. Dr. Kevin J. Folliard assisted in data interpretation of Chapters 2. Dr. Michael D.A. Thomas assisted on the data analysis and interpretation of Chapter 2.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF FIGURES

TABLE OF FIGURES (Continued)

TABLE OF TABLES

1   General Introduction

1.1   Scope and Layout of this Thesis

This Master of Science thesis follows the manuscript option as described in the OSU Graduate School Thesis Guide 2010-2011 and covers a series of tests to determine the ability and resulting effects of using fly ash as a means of decreasing alkali-silica reaction. Two technical papers with original content were developed and are introduced below. These publications and the associated research provide the proper background upon which a rapid test method to accurately determine the alkali contribution from fly ash to the pore solution of concrete can be developed. This thesis is structured as follows:

Chapter 1: *General Introduction* – This chapter provides a basic description of the alkali-silica reaction and the ability of fly ash to control the deleterious reaction. Also, the need to accurately assess the availability of alkali from SCMs is of paramount importance to the research.

Chapter 2: *Manuscript* 1 - The title of the first technical paper is "Influence of Alkalies from Fly Ash to Pore Solution: ASR Considerations." This manuscript summarizes a series of tests run to determine the effectiveness of various fly ashes to mitigate ASR-induced expansion. Also discussed are the applied results of a chemical index introduced by Malvar et al., which strives to utilize calculations based on raw fly ash chemical constituents and ASTM C 1260 expansion results to determine the appropriate fly ash replacement level to mitigate ASR expansion. Strengths and weaknesses of the chemical index method are presented. Additional data collected for this paper are presented in Appendix A. This manuscript will be submitted to the *ACI Materials Journal* in November 2010.

Chapter 3: *Manuscript 2* - The second technical paper entitled "Fly Ash and the Mitigation of Alkali-Silica Reaction: Alkali Availability", discusses three procedures performed in an effort to better determine the alkali contribution from fly ash to the concrete pore solutions. The first involved making a series of cement-fly ash paste

samples with varying replacement levels and types of fly ashes which were cured for a set period of time at a particular temperature before the pore solution was extracted using a specialized die. After extraction the solutions were chemically analyzed to determine the alkali and calcium concentrations. Part two related the pore solution chemistry determined from part one to expansion data collected from a series of ASTM C 1567 accelerated mortar bar tests. The tests were performed on samples made with varying replacement levels of the same fly ashes studied in part one and the effectiveness of the fly ashes to mitigate ASR expansion was related to the pore solution data previously collected. Part three involved casting a series of paste samples, which, upon reaching a predetermined curing time were crushed and soaked in solutions of increasing alkalinity for a discrete timeframe. At that time the solutions were chemically analyzed to determine the alkali leaching characteristics of the particular mixture. Data collected from these procedures are presented in Appendix B of this document. This technical paper will be submitted to *Cement and Concrete Research* in November 2010.

Chapter 5: *General Conclusion* - This chapter summarizes the goal of this research project and provides the overall conclusions from the two manuscripts. Future work based on this research is also discussed.

1.2   Background and Introduction

Alkali-silica reaction (ASR) is one of the leading causes of concrete deterioration worldwide, second only to corrosion of steel (reinforced/pre-stressed/post-tensioned) in concrete. This reaction takes place internally in concrete between reactive aggregates and the hydroxyl ions and alkalies of the pore solution. Three conditions are necessary for ASR to occur: (1) available alkalies in pore solution; (2) reactive silica present in the aggregates; and (3) sufficient moisture available to drive the reaction. When all three of these conditions are met, a gel-like material, rich in alkalies, silica and other ions is formed in and around aggregates as well as within the pores of the concrete. This gel has a high affinity to absorb water molecules also present in the surrounding pore solution (emanating from either internal or external sources). As water is absorbed the gel expands, exerting tensile forces in the concrete matrix. When the expansive pressure exceeds the tensile capacity of the concrete, cracking may occur. Once cracking occurs, external water can more easily penetrate the concrete, thereby exacerbating ASR and increasing the potential for other durability mechanisms, such as corrosion, sulfate attack or freeze-thaw attack to further deteriorate the concrete. Figure 1.1 displays a crack formed from ASR in a concrete footing exposed to outdoor conditions in La Grange, Texas.

Figure 1.1–Severe ASR crack in concrete slab[1]

Eliminating any of the three conditions necessary for ASR (sufficient alkalies, reactive silica provided by the aggregates, and available moisture) may effectively minimize or even eliminate ASR and damage due to ASR-related expansion. However, it may be challenging and in fact impossible to eliminate all or even any of these conditions. As a result, much attention has been focused in the past 70 years on mitigation strategies to eliminate or at the very least, reduce the risk of deleterious ASR. Typical mitigation strategies may involve the use of supplementary cementitious (or cementing) materials (SCMs), such as fly ash, silica fume, ground granulated blast furnace slag, metakaolin, rice husk ash and other natural pozzolans. To a lesser extent chemical admixtures, mainly lithium-based salts, have also shown promise and have been used effectively to control ASR in fresh concrete.

Of particular interest is the use of fly ash as an SCM as it improves the workability of fresh concrete, strength and long-term performance of hardened concrete, and the recycling of this material has multiple environmental benefits. Additionally, it has been understood for over 60 years that fly ash can effectively control ASR-induced damage, however, there remain many questions about the efficacy of fly ash, in particular "border-line" ashes for use as SCMs to control deleterious ASR. One of the most pressing issues centers on the alkali contribution of the fly ash to the concrete pore solution. Although SCMs, and fly ash in particular, are effective at mitigating ASR, they also contain a certain amount of alkalies, sometimes at even higher percentages than the portland cement they replace. Some of those alkalies may be tied up in crystalline products and thus not available for reaction with the aggregates. However, there are currently no test methods for accurately and rapidly determining the alkali availability from fly ash. Therefore, due to this inability to determine the alkali contribution from fly ash, many ashes have been precluded from beneficial use in concrete. A reliable test method that can detect available alkalies from fly ash in a reasonable timeframe is needed to increase the use of fly ash as a supplementary cementing material.

1.2.1   Cement Chemistry Notation

The products of the reaction between cement and water are called the "hydration products". The two primary products are listed below and will be referenced throughout this document.

C-S-H – Calcium silicate hydrate [$3CaO \cdot 2SiO_2 \cdot 8H_2O$]

C-H – Calcium hydroxide [$CaO \cdot (OH)_2$]

The primary reaction product is C-S-H, which is also the main source of concrete strength. The structure of this product ranges from poorly crystalline to amorphous and occupies 50-60% of the solid volume of the hydrated cement paste. The strength provided by this product is due to covalent/ionic bonding as well as Van der Waals bonding within the complex structure. Calcium hydroxide, or C-H, occupies only 20-25% of the solid volume in the hydrated cement paste and does not contribute much to the concrete strength.[2]

1.2.2   Alkali-Silica Reaction: Basics

Alkali-silica reaction has been a known cause of concrete deterioration for over 70 years. Since its discovery in the late 1930s by Thomas Stanton of the California Division of Highways, ASR has been observed as a leading cause of premature concrete deterioration throughout the world.[3] Although the factors that lead to deleterious ASR are commonly agreed upon, the mechanism by which the alkali-silica gel causes expansion and subsequent cracking in concrete is not yet entirely understood by researchers in the field.

Alkali-silica reaction is a chemical reaction that is the result of hydroxyl ions attacking certain siliceous minerals in fine or coarse aggregates. The silica that is liberated then combines with alkalies (Na^+ and K^+) that are present in the concrete pore solution to ensure charge balance. The resulting alkali-silica gel then imbibes water and expands, which may result in cracking of the aggregates, cement paste and ultimately the concrete. It is widely accepted that in order for alkali-silica reaction to cause damage in concrete three components are necessary: sufficient alkalies, reactive silica, and adequate moisture.

Alkalies

The alkalies (Na^+ and K^+) are typically supplied by the portland cement. However, supplementary cementing materials (SCMs), chemical admixtures, and external sources such as seawater, deicing salts and anti-icing chemicals can also contribute to the alkalinity of the pore solution. In fact certain aggregate species, particularly those containing feldspars may also release alkalies to the pore solution.[4]

The amount of alkali in cement is typically referred to as a sodium oxide equivalency and written Na_2O_{eq}. The following equation is used to determine the sodium oxide equivalency of the portland cement:

$$Na_2O_{eq} = Na_2O + 0.658\ K_2O \qquad\qquad \textbf{Eq 1.1}$$

Where: Na_2O_{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 alkalies in portland cement is relatively low in comparison to other compounds and oxides; generally ranging between 0.2 to 1.3 percent. Initial research on ASR proposed that expansion due to ASR was unlikely to occur when the percentage of alkalies in the cement fell below 0.6 percent Na_2O_{eq}.[3] This approach has since been used as a mitigation option to limit ASR in new concrete; however, it has been concluded that reducing the percent contribution of alkalies from portland cement is not, on its own, an effective method of mitigating ASR for all reactive aggregate types as this approach does not limit the total alkali content (or alkali loading) of the concrete (although it can lower it).[4] Additionally, certain aggregates with very low pessimum proportions may react even at low alkali loadings. Within the pore solution of concrete the alkalies disassociate in solution leaving K^+ and Na^+ which must then be balanced by hydroxyl ions, or OH^- ions, in order to maintain charge equilibrium. The presence of the alkalies, and thus the equivalent concentration of hydroxyl ions, raises the pH of the pore solution.

For ASR to occur the pH must reach between 13.2 and 13.8, making it the trigger of the reaction.[4]

Reactive Silica

Reactive silica is amorphous or disordered silica found in certain aggregates. This poorly crystalline silica is more susceptible to ASR than well-crystallized or dense forms of silica due to its increased solubility; thus amorphous silica dissolves more readily in the high pH of the pore solution of concrete. The degree of reactivity of aggregate(s) depends on a number of factors, including the mineralogy of the aggregate, the crystallinity of the silica and its solubility. Common reactive minerals susceptible to ASR include strained quartz, cristobalite, opal, obsidian, chert, and obsidian.[5]

Adequate Moisture

Adequate moisture, the third and final necessary component for ASR to occur, is one of the key components in the expansion of the gel once formation has occurred. Water is found within the pore solution of concrete and is also introduced from external sources. A minimum relative humidity of 80 percent has been reported to provide enough moisture to drive the expansion of the alkali-silica gel and sustain the reaction.[4, 6]

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 hydrate (C-S-H), as well as other hydration products (ettringite, calcium monosulfoaluminate, etc.). The calcium from the formation of these products (in particular 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 available calcium is required to promote expansion due to ASR.[7] 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.[7] Although the role calcium plays on gel expansion remains unclear, a series of mechanisms have been proposed, as listed below:

- Calcium may replace alkalies in the reaction product thereby regenerating alkalies for further reaction (alkali recycling)[7, 8]
- CH may act as a buffer maintaining a high level of OH⁻ in solution[7, 9]
- High calcium concentrations in the pore solution prevent the diffusion of silica away from reacting aggregate particles[7, 10, 11]
- If calcium is not available reactive silica may merely dissolve in alkali hydroxide solution without causing damage[7, 12]
- 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[7, 13, 14]

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 alkalies, further improving the resistance of concrete to deleterious ASR.

1.2.3   Alkali-Silica Reaction and the Mechanism of Gel Formation

The term *alkali-silica reaction* is somewhat misleading as the actual reaction initially occurs between the hydroxyl (OH⁻) ions of the pore solution and the reactive siliceous aggregate. The high concentration of the hydroxyl ions in the pore solution is equal to that of the alkali cations in order to maintain charge equilibrium. It is this high OH⁻ concentration that causes the high pH which, in turn, leads to the initial breakdown of the reactive silica in the aggregate.[4] The process begins with the attack of the hydroxyl ions on the surface of the siliceous aggregate, leaving acidic silanol (Si-OH) groups, as depicted by Equation 1.2. Additional OH⁻ ions continue to penetrate the aggregate, breaking down silanol groups further into SiO⁻ molecules as Equation 1.3 represents. The negatively charged SiO⁻ molecules attract the positively charged cations (Na⁺ and K⁺) of

the pore solution, which bind to form Si-O-Na, shown in Equation 1.4.[4, 7] Equations 1.2-4 involve sodium (Na) as a cation, however, in actuality it is the potassium (K) ions that are dominant in modern cements and the commensurate reaction with K as the cation follows.

$$H_2O + Si\text{-}O\text{-}Si \rightarrow Si\text{-}OH + OH\text{-}Si \qquad \textbf{Eq 1.2}$$
$$Si\text{-}OH + OH^- \rightarrow Si\text{-}O^- + H_2O \qquad \textbf{Eq 1.3}$$
$$Si\text{-}OH + Na^+ + OH^- \rightarrow Si\text{-}O\text{-}Na + H_2O \qquad \textbf{Eq 1.4}$$
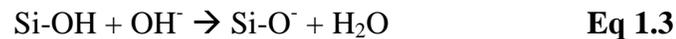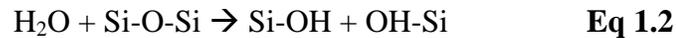
The resulting Si-O-Na material comprises the alkali-silica gel which is induced at the pore-aggregate interface and expands around the surface of the aggregate and within the aggregate itself inside preexisting microcracks. The rate and amount of gel formation is governed by the alkalinity of the pore solution as well as the crystallinity of the silica in the aggregate.[4]

Although the mechanisms behind the formation of ASR gel are well understood, the mechanism for expansion of the gel remains uncertain. Four prevailing theories have emerged over the past 70 years to explain the mechanism of gel expansion, all with common agreement that water is the main component driving the expansion process. The four theories of expansion include the double-layer, osmotic pressure, C-S-H-shell, and the calcium/alkali exchange theory.

Osmotic Pressure Theory

The osmotic pressure theory speculates that the cement paste surrounding the reactive aggregates acts as a semi-permeable membrane, blocking the large silicate ions from exiting while allowing the water and both the ions and molecules of the alkali hydroxides to diffuse through. Under these conditions the alkali silicate formed on the surface of the aggregate particle draws solution through the cement paste and alkali silica gel continues to form. As the gel continues to swell an osmotic pressure cell is formed and increasing hydrostatic pressure is applied on the cement paste, eventually resulting in cracking.[15]

C-S-H Shell Theory

This theory hypothesizes that in the presence of calcium hydroxide, alkali ions from alkali salts and hydroxyl ions from $Ca(OH)_2$ enter into the aggregate matrix of reactive silica leaving calcium and anions in the pore solution. The penetration of the solvated hydroxyl and alkali ions causes the Si-O-Si bonds of the reactive aggregate to break apart which, in turn, opens the grains for further penetration of ions and allows for the release of some SiO_2 into the pore solution. As the solvated hydroxyl and alkali ions infiltrate into the aggregate grains, calcium, hydroxyl and water molecules also migrate into the reactive siliceous material. When high concentrations of $Ca(OH)_2$ and alkali salts are present in the pore solution, only a limited amount of SiO_2 can diffuse out while more materials penetrate into the aggregate structure. This imbalance results in an expansive force within the aggregate grain. If, however, the $Ca(OH)_2$ and alkali salt concentrations are low, the rate of penetration of the hydroxyl and alkali ions is low while the migration of SiO_2 is increased, thus resulting in a lower expansive force.[16]

Calcium/Alkali Exchange Theory

The calcium/alkali exchange theory also considers calcium an essential component to the expansion of alkali-silica gel. This theory hypothesizes that the alkali-silica gel imbibes Ca^{2+} ions and, in turn, exchanges them for alkali ions which then react with the pore solution to increase pH, attack silica species in aggregates and thus create more alkali-silica gel. As more gel is formed, tensile stresses increase, more space is utilized and cracking then occurs in order to accommodate the gel expansion. The ion and water uptake is governed by the temperature and moisture conditions of the material and thus is coupled to physical transport processes.[17]

Double-Layer Theory

The double-layer theory suggests that the expansion of the gel is attributed to swelling caused by electrical double-layer repulsive forces. When a liquid and a solid come into contact, the surface of the solid material carries excess charge, which electrifies the interface. This excess charge alters the properties of both the physical and liquid

materials. ASR involves the interaction of the highly-charged silica aggregate surface with the alkaline pore solution of the concrete. This is the reaction that leads to the breakdown of the silica and the formation of the alkali-silica gel. Within the gel, negatively charged solid silica particles attract positively charged cations which thus bind to form a "rigid layer" around the solid particle. Surrounding this rigid layer a "diffuse layer" is formed comprised of more cations and anions found within the gel.[18] Thus the electrical double layer is composed of sodium, potassium, and calcium ions which surround the negatively charged silica surface. Once this double layer has been established, water is taken in, causing the size of the external layer to increase around the particle. As water is introduced into the layer, electrostatic forces predominate and particles are pushed apart as the gel grows.[18]

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.

1.2.4 ASR Test Methods

A variety of test methods to detect alkali-silica reactivity in aggregates have been developed over the past 70 years since ASR was first discovered. Most recently several of these test methods have been modified to allow for testing the efficiency of mitigation options including supplementary cementitious materials and/or chemical admixtures. While a summary of all ASR testing methods is beyond the scope of this current research project and review, it is important to highlight those methodologies which provide the most accurate and reliable results. Some of these methodologies were used throughout

the current research project both for detecting aggregate reactivity as well as determining the most effective mitigation techniques.

Table 1.1 below provides a detailed outline of the recommended test methods according to ASTM and CSA standards. A brief description and expansion limits are given. A more detailed explanation of the testing methods used in this research project is given in the following table. The ASTM versions of these methods were followed in this project unless otherwise stated.

Table 1.1 Recommended Test Methods According to ASTM and CSA Standards

Petrographic Examination			
ASTM C 295: Standard Guide for Petrographic Examination of Aggregates for Concrete	CSAA23.2-15A: 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 *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)	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. Expansion between 0.10% and 0.20% may indicate deleterious or innocuous behavior, supplementary information required 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

Table 1.2 Recommended Test Methods According to ASTM and CSA Standards (Continued)

ASTM C 1567-08: Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)	*CSA A23.2-28A:* Standard practice for laboratory testing to demonstrate the effectiveness of supplementary cementing materials and lithium-based admixtures to prevent alkali-silica reaction in concrete *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)	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.	*ASTM C 1567-07:* 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, supplementary testing in ASTM C 1293 should be performed CSA-A23.2-27A: After 16 days, Exp < 0.150% indicate combinations of SCMs that will mitigate ASR effectively Exp > 0.150% indicate combinations of SCMs that may produce deleterious expansion in concrete
Concrete Tests			
ASTM Test Method	**CSA Companion**	**Description**	**Expansion Limits**
ASTM C 1293-08b: Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction	*CSA A23.2-14A:* Potential expansivity of aggregates (procedure for length change due to alkali-aggregate reaction in concrete prisms at 38 °C) *CSA-A23.2-27A:* Standard practice to identify degree of alkali-reactivity of aggregates and to identify measures to avoid deleterious expansion in concrete	Commonly referred to as the concrete prism test, this test uses high-alkali cement with boosted alkalies (1.25% Na_2O_{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.	*ASTM C 1293-08b:* Exp ≥ 0.04% at 1 year indicates potentially deleterious expansion *CSA A23.2-17A:* Exp > 0.040% at 1 year indicates potentially deleterious expansion

Table 1.3 Recommended Test Methods According to ASTM and CSA Standards (Continued)

ASTM C 1293-08b: Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction See Appendix for update, also in ASTM C 33-08	*CSA A23.2-28A:* Standard practice for laboratory testing to demonstrate the effectiveness of supplementary cementing materials and lithium-based admixtures to prevent alkali-silica reaction in concrete *CSA-A23.2-27A:* Standard practice to identify degree of alkali-reactivity of aggregates and to identify measures to avoid deleterious expansion in concrete	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.	*ASTM C 1293-08b:* Exp < 0.04% at 1 year indicates effectiveness of SCMs and/or lithium nitrate to control deleterious reaction due to ASR *CSA A23.2-27A:* Exp < 0.040% at 1 year indicates effectiveness of SCMs and/or lithium nitrate to control deleterious reaction due to ASR

ASTM C 1260 – Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)

ASTM C 1260 is a rapid test used to assess alkali silica reactivity in mortars and is often referred to as the accelerated mortar bar test (AMBT). This test involves casting mortar prisms that measure 1 in. x 1 in. x 11.25 in (25 mm x 25 mm x 285 mm). A stainless steel gage stud is cast into both ends of each bar to provide an effective gage length of 10.00 ± 0.10 in. (250 ± 2.5 mm). After curing for 24 ± 2h in a 100% relative humidity room at 73.4 ± 3 °F (23 ± 1.7 °C), the specimens are measured and submerged in tap water, then 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 ± 2h later and the bars are quickly transferred to a solution of 1 N NaOH which is already at 176 ± 3.6 °F (80.0 ± 2.0 °C). The bars then remain in the sodium hydroxide solution at the increased temperature for a period of 14 days. Many researchers extend this exposure period to 28 days. Periodic length measurements are taken throughout this time period at approximately the same time each day. Length change is recorded to the nearest 0.0001 inch and results are presented for the average of three or four mortar bars to the nearest 0.01%.[19]

Expansion criteria for this test fall into three categories within ASTM C 1260 based on expansion occurring 16 days after casting (14 days after immersion in 1 N NaOH). Expansion of less than 0.10% is generally considered to be indicative of innocuous behavior. Expansions of more than 0.20% indicate that the aggregates are potentially deleterious. Expansions that fall between 0.10 and 0.20% indicate that the aggregate may exhibit either innocuous or deleterious performance in the field.[19] The above expansion criteria, as described in the non-mandatory appendix of ASTM C 1260, are not actually used by many researchers or agencies, but rather, the consensus among many ASR researchers and engineers is a single expansion limit of 0.10% after 14 days of immersion in the soak solution.[20] However, other agencies may use stricter limits such as lower expansion limits combined with longer exposure periods to NaOH. This may be especially used for critical structures where little expansion can be accommodated or tolerated (e.g. airfield pavements, dams, concrete structures with internal mechanical features).

It is important to note that this test is only used for testing mortar. Therefore, if the reactivity of a coarse aggregate is to be assessed with this test method, the aggregate must be crushed to meet the gradation standards of the test. As a result, it is possible to expose and remove reactive phases through the crushing, sieving and washing process required by the standard.[19] This may lead to inaccurate reactivity predictions when using ASTM C 1260 for field structures containing potentially reactive coarse aggregates.

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 utilizes the same testing procedures as ASTM C 1260; however, combinations of portland cement, SCMs, and a reactive aggregate are used instead of only portland cement with a reactive aggregate. The cementitious materials are comprised of various proportions of portland cement, pozzolans and/or ground granulated blast-furnace slag (slag) or other SCMs. Pozzolans and slag may be tested in combination or

individually to determine the appropriate amount required to reduce expansion to an acceptable level.[21] The standard recommends testing the same aggregate and hydraulic cement without pozzolans or slag using Test Method C 1260 to determine base levels of reactivity. When proportioning the mortar during testing, the standard calls for the use of 1 part of cementitious materials, inclusive of hydraulic cement plus pozzolan or slag, and 2.25 parts of graded aggregate by mass for aggregates with a relative density greater than or equal to 2.45. For aggregates with a relative density less than 2.45 an adjustment is necessary to properly proportion the material and ensure proper yield.[21]

When silica fume or metakaolin are used as mitigation options in replacement of a portion of the portland cement a high range water reducer (HRWR) meeting all requirements can be used if necessary to provide sufficient dispersion and workability of the concrete mixture. However, the water-cementitious materials ratio must remain at 0.47 by mass and the contribution of additional alkalies supplied by the HRWR must be considered.[21, 22]

ASTM C 1293 – Standard Test Method for Concrete Aggregates by Determination of Length Change of Concrete Due to Alkali-Silica Reaction (Prism Test)

The ASTM C 1293 test is considered a more reliable test method than the ASTM C 1260 test as it tests a larger specimen, uses a full scale concrete mixture, and the testing environment is far less harsh than ASTM C 1260.[23] This test is generally referred to as the concrete prism test (CPT). In this test, concrete prisms are cast with square cross sections of 3.00 ± 0.03 in. (75.0 ± 0.7 mm) and are 11.25 in. (285 mm) in length. Stainless steel gage studs are cast in both ends of each prism to give an effective gage length of 10.00 ± 0.10 in. (250 ± 2.5 mm). An ASTM C 150 Type I Cement with a 0.9 ± 0.1 Na_2O_{eq} is specified for this test method. Sodium hydroxide solution is added to the mixing water, as specified by ASTM C 1293, to raise the alkali content to 1.25 Na_2O_{eq}. Prisms are demolded after 23.5 ± 0.5h and are measured for an initial reading. Prisms are then stored at 100.4 ± 3.6 °F (38.0 ± 2.0 °C) for a period of 1 year for concrete containing no SCMs.[23] Although the current version of ASTM C 1293 does not cover the use of

SCMs within this test method, it is included in the Canadian Standards Society (CSA) Test Method A23.2-28A. The storage length is increased to 2 years for mixtures containing SCMs.[24] Prior to any length change measurements prisms are brought to 73.4 ± 3.6 °F (23 ± 2.0 °C) for 16 ± 4h. Length change measurements are performed at 1, 4, 8, 13, 26, 39 and 52 weeks; additional readings are taken at 78 and 108 weeks for mixtures containing SCMs.[23, 24]

Expansions are recorded to the nearest 0.0001 in. and the average of at least three prisms (often four are cast) for each test is reported to the nearest 0.001%. Expansion criteria, as stated in the non-mandatory appendix of the standard, indicate that a concrete mixture with expansion equal to or greater than 0.04% at one year is to be considered potentially deleteriously reactive.[25] This test method can also be used to determine the efficacy of using SCMs and/or chemical admixtures, namely lithium nitrate, to mitigate deleterious ASR. The expansion limit is retained at 0.04% at 2 years of age for prisms incorporating mitigation measures.[24]

ASTM C 295 – Standard Guide for Petrographic Examination of Aggregates for Concrete

ASTM C 295 outlines procedures for the petrographic examination of aggregate samples and raw materials for use in such aggregates which are considered for use in concrete. This guideline summarizes the selection of properties that should be looked for, the petrographic techniques that ought to be used, and the manner in the which the techniques should be performed.[24]

The exact petrographic examination procedures will depend on the purpose of the examination as well as the composition and nature of the sample itself, though most cases will utilize optical microscopy. Other procedures, such as X-ray diffraction (XRD) analysis, differential thermal analysis (DTA), infrared spectroscopy, scanning electron microscopy (SEM), or energy-dispersive x-ray analysis (EDX) can be employed for particular purposes or to investigate particular problems. Generally, it is necessary to identify the constituents of a sample in order to determine the behavior of the material in

its intended use. As stated in the standard, the four main purposes of the petrographic analysis include:

1) To determine the physical and chemical characteristics of the material that may be observed by petrographic methods and that have a bearing on the performance of the material in its intended use

2) To describe and classify the constituents of the sample

3) To determine the relative amounts of the constituents of the sample that are essential for proper evaluation of the sample when the constituents differ significantly in properties that have a bearing on the performance of the material in its intended use, and

4) To compare samples of aggregate from new sources with samples of aggregate from one of more sources, for which test data or performance records are available.[24]

The petrographic examination should determine whether the particular aggregate consists of chemically unstable minerals such as unstable sulfides that may form sulfuric acid, soluble sulfates, or volumetrically unstable materials such as smectites. This analysis should also identify the portion of each coarse aggregate that is composed of altered or weathered particles as well as the extent of the weathering. Examinations may be used to determine the amounts of cubic, spherical, ellipsoidal, pyramidal, tabular, flat, and elongated particles within an aggregate sample which helps to determine the water demand of the concrete mixture. Also, the petrographic examination should identify and quantify potentially alkali-carbonate and alkali-silica reactive constituents as well as recommend additional tests to prove the presence of these materials. As listed in the standard, alkali-carbonate reactive rocks include calcareous dolomites or dolomitic limestones with clayey insoluble residues, whereas alkali-silica reactive components include opal, cristobalite, tridymite, siliceous and some intermediate volcanic glass, chert, glassy to cryptocrystalline acid volcanic rocks, synthetic siliceous glasses, some argillites, phyllites, metamorphic greywackes, rocks containing highly metamorphic

quartz such as greywackes, phyllites, schists, gneisses, gneissic granites, vein quartz, and sandstone.[24]

ASTM C 856 – Standard Practice for Petrographic Examination of Hardened Concrete
ASTM C856 outlines the procedures for the petrographic examination of samples of hardened concrete which may be taken from concrete constructions, may be portions of or complete concrete products, or they may be concrete or mortar specimens that have been exposed in natural environments, or to simulated service conditions, or subjected to laboratory tests. The petrographic procedures discussed in the standard are applicable for samples of all types of hardened hydraulic-cement mixtures, inclusive of concrete, mortar, grout, plaster, stucco, terrazzo, etc.[26]

The purpose of ASTM C 856 is dependent on the source of the concrete under examination. For concrete from construction detailed determination of the condition of the concrete is a primary purpose. However, other purposes of the examination include, but are not limited to: identification of the causes of poor quality, distress, or deterioration; determination of the probable future performance of the concrete; description of the cementitious matrix, including examination of the kind of hydraulic binder used, degree of hydration, degree of carbonation, evidence of unsoundness, presence of mineral admixture, nature of the hydration products, adequacy of curing, and unusually high water/cement ratio of the paste. Another primary purpose is to determine whether alkali-silica or alkali-carbonate reactions have taken place between the contaminants and the matrix and their severity if present.[26] The purpose of performing a petrographic examination of laboratory specimens is to establish whether alkali-silica, alkali-carbonate reaction, or any other cement-aggregate reactions occur, which aggregate constituents were most effected, what evidence of the reaction exists, and what effects the reaction has on the concrete.[26]

A designated annex of this standard outlines a uranyl acetate method for determining potential locations of alkali-silica gel. It is required that the substances in those particular locations must be identified using more definitive techniques, such as petrographic

microscopy.[26] The technique to determine potential alkali-silica gel locations involves treating the surface of conditioned concrete with a solution of uranyl-acetate which is then exposed to a short-wave ultraviolet light, causing fluorescence. Silica fume, fly ash, and other pozzolanic materials have the potential to react and create secondary products similar to alkali-silica gel and if these products are distributed evenly, a uniform background is created on which the more concentrated and localized alkali-silica gel can be distinguished.   However, materials containing opal and potentially other rock components can also be detected, as well as localized concentrations of secondary ettringite. In addition, due to health and safety concerns associated with the use of uranyl acetate, this test is generally avoided. Therefore, if alkali-silica gel is thought to be present in a sample, further tests are required.

A second staining method, developed at Los Alamos National Research Laboratory, exploits the structure and composition of the ASR gel, namely the open structure which allows cation and fluid exchange, as well as the mineral composition of the material.[27] As mentioned previously, although ASR gels contain appreciable concentrations of sodium, most ASR gels are dominated by the alkali cation potassium. Thus, the technique outlined by the Los Alamos Laboratory primarily distinguishes potassium and would require modifications in order to be effective on gels highly enriched in sodium and depleted of potassium. Two stains are used in the treatment process derived at Los Alamos. The first, a saturated aqueous solution of sodium cobaltinitrite [$Na_3Co(NO_2)_6$], reacts with soluble potassium to produce a yellow precipitate, thereby staining potassium-rich ASR gel. The second stain, a saturated aqueous solution of one of several rhodamine compounds, reacts with components in concrete other than potassium-rich ASR gel, turning them a pinkish color. The use of this second stain is in part to highlight the areas of the yellow-stained ASR gel by providing a contrasting background, as well as to identify other degradation products.[27]

1.2.5   Specifications

The research conducted for this thesis was sponsored by the Naval Facilities Engineering Command - Engineering Service Center (NAVFAC-ESC), Port Huenimie, California. As a result a brief discussion of their guidelines for concrete construction, and in particular alkali-silica reaction, is outlined below.   The Unified Facilities Guide Specification (UFGS) 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. [28] 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.[28]   The procedures of this project adhered to the requirements described by the Unified Facilities Guide Specifications to ensure consistency with ongoing concrete guidelines. With respect to ASR mitigation, the UFGS specification limits accelerated mortar bar expansion to 0.08% after 28 days. Therefore, with blended mixtures it is required to use enough SCM to lower expansion to be equal to or less than 0.08 percent after 28 days of immersion in 1N NaOH solution.[29]

1.2.6   Mitigating ASR in Concrete

The most common strategies for mitigating ASR in new concrete include limiting the alkali content of the concrete, using nonreactive aggregates, incorporating SCMs and/or the use of chemical admixtures, namely lithium compounds.

Using nonreactive aggregates is certainly the most effective method of preventing ASR because without reactive silica the reaction cannot take place. However, nonreactive aggregates may not represent a viable economic option nor are they generally available in many areas of the United States. Also, to confirm that an aggregate is nonreactive involves strict testing of the aggregate material, good quality control, and successful field performance documentation. Standard tests for reactivity include ASTM C 1260 and

ASTM C 1293 which were discussed in the previous section. If all of the conditions are met the aggregate can be used without additional precautions. Otherwise, it may be necessary to take extra precautions such as replacing cement with suitable SCM(s) and/or addition of chemical admixture to the concrete to limit the risk of deleterious ASR.

The use of lithium compounds to control damage due to ASR has also increased in popularity in the past 10 years, following a lull in the research community and industry for using this type of mitigation option. However, the mechanisms behind lithium's ability to reduce expansion in concrete are yet to be clearly understood. Multiple theories have been presented attempting to explain the phenomenon behind the success of lithium utilization to mitigate ASR, though this remains a prime subject for future research.[4, 30-33]

1.2.7   Supplementary cementing materials (SCMs)
SCMs are materials that are added to or used in place of ordinary portland cement and contribute to the properties of hardened concrete by means of pozzolanic and/or hydraulic cementing activity. SCMs are typically incorporated in concrete mixtures to improve workability, control setting time, enhance strength development, reduce permeability, reduce the potential for acid and sulfate attack, decrease corrosion of reinforcement and suppress alkali-silica reaction and related expansion.[34]

The most common SCMs include fly ash, silica fume, ground granulated blast furnace slag (GGBFS), and natural pozzolans such as metakaolin and rice husk ash. These SCMs are used for different applications and in varying dosages depending on the physical makeup as well as the effect of the desired concrete material. Necessary physical characteristics of the most common SCMs as well as portland cement are provided in Table 1.4. Also included in this table are typical replacement dosages to control ASR.

Table 1.4. Physical Properties of Ordinary Portland Cement and Common SCMs

Material	Specific gravity	Surface area (m²/kg)	Bulk density (kg/m³)	Particle diameter (μm)	% 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	15-40	Tan
Fly Ash - Class F	1.9-2.8	300-500	540-860	1-100 avg: <20	15-40	Brown
Silica Fume	2.20-2.5	20,000	130-430	<1 avg: 0.1	5.0-10	Black
Slag	2.85-2.95	400-600	1050-1375	<45	30-50	White
Metakaolin	2.40-2.61	650-1350	300-400	1.0-2.0	7-35	White
Rice Husk Ash	2.06	360	450-600	5.0-10	5.0-40	Off-white

Sources:[34-39]

Table 1.5 presents the effect on different concrete qualities due to the use of individual SCMs. Comparing the effects resulting from the use of particular SCMs makes it possible to consider ternary blends, using two SCMs to create a concrete with desired properties. A "-" indicates a negative effect and a "+" sign represents a positive effect.

Table 1.5. SCM Reactivity and Effects on Fresh and Hardened Properties

Material	Workability	Early-Age Strength	Long-term Strength	ASR Mitigation
Silica fume	--	++	+++	+
Class C Fly ash	++	+++	++	+
Class F Fly ash	++	-	++	+++
Metakaolin	-	+	++	+++
GGBFS	negl	-	++	++
Rice Husk Ash	+	+	+	++

Supplementary cementing materials with hydraulic properties chemically react with water to form hydrated compounds with cementing properties. These SCMs include ground granulated blast furnace slag (GGBFS), Class C fly ash, natural cement or cement rock, and hydraulic hydrated lime. SCMs with pozzolanic activity are highly siliceous or alumino-siliceous materials which, at ordinary temperatures, when crushed finely and in the presence of water, react chemically with the calcium hydroxide that is formed by the hydration of portland cement, thus forming cementitious compounds, namely C-S-H. SCMs with pozzolanic activity include Class F fly, silica fume, metakaolin, clay and shale. If ground finely enough, certain sources of silica may also react pozzolanically.

This may include alkali-silica reactive aggregates and commercially produced waste glass sources.[40]

Supplementary cementing materials can typically be classified as either by-product materials or natural materials. By-product materials consist of the materials that are not the primary products of the particular manufacturing industry which may or may not require processing before being mixed with the cementing material. Natural materials used as SCMs are materials that are acquired and processed specifically for the purpose of making concrete. Typical processing of these materials includes grinding, crushing, size separation and/or thermal activation.[5] The use of industrial by-products has become the primary source of SCMs in concrete due to their availability, environmental sustainability and economic benefits. Natural pozzolans are still common in many parts of the world.[5]

The use of SCMs is the most common ASR mitigation strategy. SCMs must be properly specified and concrete made with SCMs is more susceptible to mistreatment which may result in increased scaling from deicer salt application if not finished properly. ACI 318-08 has maximum requirements for SCM use in concrete exposed to freezing-and-thawing and in continuous contact with moisture and exposed to deicing chemicals, as shown in Table 1.6.

Table 1.6: Requirements for concrete subject to severe conditions

Cementitious Materials	Maximum percent of total cementitious materials by weight
Fly ash or other pozzolans conforming to ASTM C 618	25
Slag	50
Silica Fume	10
Total of fly ash or other pozzolans, slag, and silica fume	50
Total of fly ash or other pozzolans and silica fume	35

Source: [41]

High levels of SCM replacement are even more subject to misuse and could lead to potential for increased carbonation which is undesirable in reinforced concrete structures.[42] When used in the appropriate proportions, SCMs can effectively reduce expansion due to ASR in three ways: reducing the available alkalies in the pore solution due to a lower concentration available from the supplementary material than in portland cement; binding alkalies in from the pore solution in hydration products, making them unavailable to react with the aggregate; and lowering the permeability of the material thus resulting in a decrease of water infiltration and movement.[43] The most commonly used SCMs include ASTM C 618 class C or class F fly ash, ASTM C 989 ground-granulated blast-furnace slag (GGBFS), ASTM C 1240 silica fume, and combinations of SCMs which are referred to as ternary blends.

1.2.8   Fly Ash

Background

A by-product of the coal burning industry, fly ash is one of the most widely used supplementary cementing materials. Collected as an off-gas with bag filters or electrostatic precipitators, fly ash is comprised of uncombusted mineral impurities from the coal which fuse together and solidify as they are transported from the combustion chamber and cooled. Depending on the type of coal burned, fly ash is divided into different classifications, distinguished by its chemical composition (based on CaO in CSA standards and the sum of $Fe_2O_3+Al_2O_3+SiO_2$ in ASTM standards). Also, the particle size distribution, morphology, and surface characteristics of fly ash have a significant effect on the water demand of the concrete mixture as well as the workability of the fresh material, and rate of strength development of hardened concrete.

Fly ash is not only beneficial because of its improvement to concrete durability, but also because it plays a role in increasing sustainability through reclamation of fly ash which would otherwise be land filled. With respect to ASR control, issues regarding the efficiency of fly ash include the dosage applied, chemical/mineralogical composition of the ash, reactivity of the aggregate, and the alkali content of the concrete.

Benefits of Fly Ash in Concrete

Benefits resulting from the use of fly ash as a supplementing cementing material 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[34, 44]

Challenges of Fly Ash in Concrete

Although the use of fly ash as a supplementary cementing material is becoming increasingly more popular, some fly ashes cannot be recycled in this manner because of the requirements set by ASTM C618, ASTM C311 or affiliated standards. ASTM C618 provides the physical and chemical specifications for coal fly ash as well as raw or calcined natural pozzolans which are intended for use in concrete. The testing methods for determining these parameters are outlined in ASTM C311. However, many fly ashes are rejected from use as a supplementary material due to reliability issues of the testing methods. Determining the 'true' alkali contribution from fly ash is one of the leading setbacks in the use of this particular SCM because to date a reliable and time effective testing method has not been established. Development of a rapid testing method for determining the chemical characteristics resulting from use of fly ash in concrete will undoubtedly assist in eliminating many of these challenges, in turn escalating the overall use of the supplementary cementing material in concrete.

Current Use

Fly ash is just one of several coal combustion products. Other products include: flue gas desulfurization (FGD) materials, bottom ash, boiler slag and other by-products. The American Coal Ash Association estimates that approximately 40% of these materials are used beneficially with the remaining ~60% being land filled. Fly ash is mainly used as a replacement for portland cement or for clinker in the manufacture of portland cement. Other uses include incorporation into building materials such as grout and cellular concrete, use in asphaltic concrete, soil stabilization, fill material, and as filler in wood and plastic products as well as paints and metal castings. FGD materials may be used in the production of synthetic gypsum and for enhancements to soil for crop production. Bottom ash or boiler slag can be used in the raw feed for portland cement production as well as geotechnical applications including structural fill and land reclamation. Boiler slag may also be used as blasting grit and roofing granules.[45]

Fly Ash Classification

Class F fly ash typically contains less than approximately 15 percent CaO, and is generally produced from the combustion of anthracite and bituminous coals. These ashes are comprised primarily of aluminosilicate glass, though some crystalline minerals including quartz, mullite and hematite are present, resulting in a decrease of the pozzolanic activity of the ash.[5] Typically added in dosages of 15% to 25% by mass of cementitious material, Class F fly ash lacks early-age strength qualities, but can significantly enhance the long term strength of the concrete. Class F ashes are characterized as having mainly pozzolanic properties.[34, 46]

Fly ash with CaO contents greater than about 15% are considered high calcium or Class C fly ashes which are products of the combustion of lignite and subbituminous coals.[46] In contrast to Class F ashes, most of the calcium of Class C ashes is in the form of reactive crystalline compounds, thus making this type more reactive. These ashes typically possess better early-age strength qualities. Class C fly ash is commonly used in dosages of 25% to 40% by mass of cementitious material, which, similarly to Class F fly

ash, depends greatly on the reactivity of the ash and the desired effects on the concrete.[34]   Class C ashes possess both hydraulic cementing as well as pozzolanic properties.

Low-calcium fly ashes are generally more effective in controlling ASR and related expansion than high-calcium ashes due to a higher concentration of silica which decreases the calcium to silica atomic ratio (Ca/Si) in the C-S-H structure.[4] This low Ca/Si ratio enhances the ability of the hydration products to bind alkalies present in the pore solution, primarily due to a negative surface charge that is imparted on C-S-H.[47] Cations, alkalies in particular, are then attracted to this negative charge and absorbed into the C-S-H structure.[4, 48] Also, low-CaO fly ashes are generally more efficient in controlling ASR expansion because the alkalies contained in the fly ash are not readily available to the concrete pore solution, and thus they are not able to participate in ASR.[4, 48]   High-CaO fly ashes tend to have more readily available alkalies, and although this class of fly ash is still effective in mitigating ASR expansion, higher dosages tend to be necessary.[4]   In addition, the C-S-H that is produced when using Class C fly ash tends to have a higher C/S ratio and tends to promote either a neutral or positive excess charge on the C-S-H, thus either having little or no affinity for absorbing cations or may even repel them.

Composition

Fly ash is primarily composed of silicate glass which contains silica, iron, calcium, alumina and minor amounts of potassium, carbon, sodium, sulfur and magnesium. The spherical shape of fly ash generally ranges in size from <1 μm to 100 μm in diameter with the majority being less than 20 μm in size.[5]   These glassy particles are mainly solid spheres, though many hollow cenospheres are also present, which together form a finely divided powder resembling portland cement to the naked eye.[34]

Reactions: Cement and Pozzolanic

Both   Class C and Class F fly ash react pozzolanically where the calcium hydroxide (portlandite) that is formed by the hydration of cement and water, reacts with the silica

from the fly ash to form calcium silicate hydrate (C-S-H). Unlike Class F fly ashes, Class C fly ashes often possess enough CaO (lime) to be self-cementing, in addition to the pozzolanic reaction with calcium hydroxide from the hydration of the cement.[49]

Replacing portland cement with fly ash not only reduces the amount of non-durable calcium hydroxide, but it helps to convert this material into more calcium silicate hydrate (C-S-H), the strongest and most durable portion of the cement paste. The increased formation of C-S-H has beneficial effects in reducing ASR, as will be discussed in subsequent sections. An additional benefit of incorporating fly ash is the combination of the small, spherically-shaped fly ash particles which improve particle packing in the cementitious paste leading to a denser paste matrix. This effect combined with the pozzolanic reaction accounts for the eventual disappearance of the interfacial transition (~50 nm zone of weaker hydrated cement paste immediately adjacent to aggregate surfaces) zone which can result in a highly durable and crack-resistant product.[44, 50]

Fly Ash and ASR Mitigation
Fly ash is the most used SCM to control alkali-silica reaction. The efficiency of fly ash in controlling the reaction depends on several parameters including:[4]

- Dosage of fly ash (typically done as a mass replacement of cement)
- Chemical composition of the fly ash (of particular importance are the lime (CaO) content, and alkali content of the ash).
- Reactivity of the aggregate source
- Chemical composition of the concrete (in particular the alkali content of the cement)

While it is not yet completely understood how fly ash mitigates ASR, research over the past 30-40 years has further elucidated several ways in which fly ash reduces this deleterious reaction. The pozzolanic reaction of fly ash with portland cement hydrates results in an increased formation of C-S-H. Researchers have shown that the increase in C-S-H (and subsequent depletion of CH) leads to a denser microstructure. The increased formation of C-S-H closes off the capillaries that allow the movement of moisture

through the concrete, resulting in lowered permeability and thus less accessibility for water to react and form alkali silica gel.[49] In addition, the C-S-H that is formed from the incorporation of fly ash (in particular lower lime ashes) is capable of enhanced long-term alkali binding which essentially traps alkalies in cement hydrates rendering the alkali unavailable to participate in deleterious alkali-silica reactions.[47, 51]

The effectiveness by which fly ash mitigates ASR expansion can be generally determined by three characteristics: fineness, mineralogy, and chemistry. Finer pozzolans have a greater ability to control expansion because of reduced permeability of the matrix which thereby decreases the penetration of water into the system. The mineralogy of the fly ash is essential because in order to mitigate ASR expansion, the chemical components must be properly bound and/or able to chemically react with the other constituents. The chemical components of the fly ash are also of importance in order to provide the correct balance of constituents necessary to prevent expansion.

Fly Ash Chemical Constituents
Calcium Oxide (CaO)

The CaO content of the fly ash is typically viewed as one of the most important parameters when assessing how well a fly ash may control ASR. Typically, as the amount of CaO increases the efficiency (at a constant replacement percentage) decreases. Therefore, higher replacements of ashes rich in CaO will be necessary to control a given reactive aggregate compared to ashes with low CaO contents. As a result, Class F fly ashes are generally more effective in controlling ASR at lower dosages (15-25%) compared to Class C fly ashes where higher dosage rates (25-40% and higher) may be necessary.

In general, low-calcium ashes are more effective in controlling ASR than high calcium ashes primarily due to a higher alkali-binding capacity. 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 lower calcium to silica ratio. The resulting C-S-H has a higher affinity

(negative surface charge) for cations, namely alkalies, which are absorbed from the pore solution.[4, 48, 52] In addition, low calcium ashes are more efficient in controlling expansion due to ASR because the alkalies provided by the ash are not readily available for reaction, whereas the alkalies contained in high-calcium ashes tend to be more readily available to the pore solution.[4, 53] As a result, higher dosages of high calcium fly ashes are needed to mitigate expansion due to ASR.[4]

Magnesium oxide (MgO)

Magnesium oxide can react in concrete to form magnesium hydroxide, which can promote deleterious expansion.[54] Previously, AASHTO M 295 (similar to ASTM C 618 and CSA A 23.5) limited the MgO content of fly ash to 5% and this limit is still enforced by the New Mexico State Highway and Transportation Department.[54-56] Typically, Class F fly ashes have very little MgO while Class C tends to have more.[54, 55, 57] However, Mehta determined that the MgO in fly ash often occurs in noncrystalline formations or in the nonexpansive mullite phase, and thus a weak correlation between expansion and magnesium oxide exists.[54, 58]

Sulfur trioxide (SO$_3$)

Both Class C and Class F fly ash have limits of 5% sulfur trioxide contents in ASTM C 618.[59] As determined by Malvar and Lenke, there is a moderate correlation ($R^2 = 0.50$) between normalized expansion due to ASR and the cementitious SO$_3$ content.[54] They purport that fly ash inhibits ASR expansion with the most significant correlations being those with MgO, SO$_3$ and the CaO/SiO$_2$ ratio.[54, 60]

Silicon dioxide (SiO$_2$)

Silicon dioxide has been known to show pozzolanic activity, and thus increased contents of SiO$_2$ has proven to increase the effectiveness of fly ash to lower expansion due to ASR.[54, 58]

Aluminum trioxide (Al$_2$O$_3$)

Alumina can contribute to the pozzolanic effect of silica, and the sum of SiO$_2$ + Al$_2$O$_3$ has shown a good correlation with pozzolanic activity.[54, 61] Thus, studies by Malvar et al., concluded an inverse correlation between normalized expansion and the cementitious Al$_2$O$_3$ content.[54]

Alkalies in Fly Ash

The effectiveness of SCMs in controlling expansion due to ASR is closely related to their ability to lower the alkalinity of the pore solution and thus decrease the concentration of one of the initial reaction products: hydroxyl or OH$^-$ ions.[52, 62] The use of fly ash increases the content of silica in the system, thus decreasing the Ca/Si ratio of the hydration products which, in turn, enhances their ability to bind alkalies, thereby reducing their availability in the pore solution. This increased alkali-binding ability affects the surface charge of the hydrates; becoming less positive and more negative as the Ca/Si ratio decreases. As the surface charge is reduced, the hydrated products attract increasing amounts of alkali cations (Na$^+$ and K$^+$).[62] Recent research has shown that in blends made with portland cement and a supplementary cementing material the alkalies from the portland cement are released relatively quickly, while the alkalies from the SCM are released over longer periods of time; the length of which is dependent on the reactivity of the particular SCM and the source of alkali within the SCM. As full hydration is approached, alkalies are released into either the solid hydrated phase, the liquid pore solution, or they remain bound in non-reactive crystalline phases.[47] It is critical to the successful application of SCMs to determine how much alkali will remain bound in either hydration products or the structure of the original SCM.

The alkalies in the pore solution have been shown to be directly correlated to the alkali, calcium, and silica content of the cementing materials. A mathematical relationship has been derived by Thomas et al. to determine the OH$^-$ or (Na$^+$ + K$^+$) concentration of the pore solution depending on the chemical composition of the cementitious blend. This relationship is expressed in Equation 1.5 below[63]:

$$OH^- = 6 \text{ x } (Na_2O_e \bullet CaO)/(SiO_2)^2 \qquad \textbf{Eq 1.5}$$

Where,

$$Na_2O_e = Na_2O + 0.658 \bullet K_2O \qquad \textbf{Eq 1.6}$$

Na_2O_e = 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 alkalies ($Na^+ + K^+$) are represented by Na_2O_e, as presented by Equation 1.6[4], which signifies the quantity of alkalies 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, alkalies from the hydrates are released to maintain equilibrium between the solid and liquid phases.[62] As the Na_2O_e of the fly ash increases, as do the amount of alkalies that are released from the ash to the pore solution, thus resulting in a pore solution of high alkalinity. Both CaO and SiO_2 affect the amount of silica and calcium 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 C-S-H decreases, resulting in increased binding capacity and ultimate reduction of alkalies from the pore solution and therefore a lower alkalinity of the pore solution.[52]

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 may release alkalies to maintain equilibrium, which are then combined in the to form the alkali-silica rich gel.[62]

ASTM C 311 "Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete", outlines and describes the chemical and physical tests that must be performed on fly ash and raw or calcined pozzolans prior to being used in portland-cement concrete. These test methods are performed to develop

data to be compared with the requirements of ASTM C 618, the Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. The physical portion of ASTM C 311 is a test of the strength of the SCM to determine whether the pozzolan or fly ash maintains an acceptable level of strength development to be sufficient for use with hydraulic cement in concrete. The chemical portion is used to help describe the chemical composition and uniformity of the material, which are not used to predict the performance of the SCM when use in concrete. Of particular interest for this project is the standard testing of available alkali from fly ash. The test procedure involves casting a fly ash and hydrated lime paste sample, storing at 38 ± 2 ^{o}C (100 ± 35 ^{o}F) for 28 days, neutralizing with dilute HCl, and determining the sodium and potassium oxides of the solution using flame photometry. The equivalent percentage of sodium oxide (Na_2O_e) can then be calculated according to Equation 1.6 as displayed previously.[64]

This test method has come under much scrutiny over the years due to its inability to correctly predict the true alkali contribution from fly ash and/or natural pozzolans to concrete pore solution.[47, 65] It is generally regarded that this test procedure is overly aggressive and accesses all of the alkali in a particular fly ash or natural pozzolan sample, thereby overestimating the *true* contribution of alkali from that material. As a result it is conceivable that many ashes are precluded from use in concrete and are often land filled, when in fact many of these ashes may perform quite well to control alkali-silica reaction in concrete and/or to provide many of the other beneficial effects of fly ash for concrete. Limits are typically placed on the total amount of alkali available from a particular pozzolanic source and it is challenging to determine where these limits should be placed since the ASTM C 311 test is overly aggressive. Conversely, many agencies perform a water-soluble version of the test where the digesting media is boiling water. This also has challenges in that the water-soluble method may not access all of the available alkali which could be realized from a given pozzolan over its lifespan in a concrete structure. This can result in an underestimation of the "true" alkali contribution and presents the less conservative, or higher risk result. Clearly, a more reliable, accurate testing method is needed to determine the true contribution of alkalies to pore solution from fly ash.

Another portion of ASTM C 311 outlines a procedure for determining the effectiveness of fly ash or natural pozzolan in controlling alkali-silica reactions. The strategy involves determining the expansion of mortar made with a mixture of at least 15% SCM replacement by mass mixed with test cement and compared by percent expansion to a control mortar made with low alkali cement in accordance with ASTM C 441. The alkali content of the control cement must be less than 0.60% while the test mixture is to have alkali content greater than that of the control mixture. Length measurements are recorded at 1 and 14 days, upon which the 14 day expansion as a percentage of the control mixture is to be recorded. A particular fly ash or natural pozzolan is consider "effective" when used at replacement levels equal to or greater than the percentages used in the test mixture with cements having alkali contents that do not exceed by more than 0.05 percentage points the alkali content of the cement used in the test mixture. Both the alkali content of the cement used in the test mixture as well as the replacement level of the SCM are functions of the effectiveness. According to the standard, the greater the level of alkalies in the test mixture cement, and the lower the percentage of fly ash or natural pozzolan, the more effective the SCM.[64] However, this test method is not recommended for testing alkali-silica reactivity of aggregates or the ability of SCMs to control the reaction due to the small sample size which results in excessive leaching of alkalies from the prisms during test and artificially low expansion values.[65]

ASTM C 618 provides the requirements upon which all classes of fly ash must conform in order to be used as a cementing material. Included in these requirements are chemical properties such as contents of silicon dioxide, aluminum oxide and iron oxide, maximum moisture contents and maximum loss of ignition. Physical requirements set by the standard include fineness, soundness, uniformity and density.[46]

1.2.9   Fly Ash Chemical Index

Recent research by Malvar and co-workers has shown promise in predicting the efficacy of fly ash to control alkali-silica reaction utilizing the accelerated mortar bar test method (AMBT). These authors demonstrated that a chemical index used to characterize a

particular fly ash and cement combination could be utilized to assess the effectiveness of that material in controlling deleterious ASR in the AMBT. They showed that the 14 day expansion in the AMBT would remain below 0.08%, with either 50% reliability (for best prediction) or 90% reliability (for safety), for a minimum cement replacement level (replacement with fly ash) determined with this chemical index. A minimum required fly ash substitution level could be determined with three different sets of inputs based on the cement chemistry, the fly ash chemistry and the 14-day AMBT results with cement only (e.g. aggregate reactivity level)[54].

In creating the chemical index, Malvar and co-workers divided the fly ash chemical constituents into two groups: those that increase expansion and those that reduce expansion. Constituents which increase expansion include CaO, Na_2O, K_2O, MgO, and SO_3, while those that reduce it consisted of SiO_2, Al_2O_3, and Fe_2O_3.[54]

As mentioned previously, CaO has been recognized as having one of the most significant effects on ASR expansion, and has often been correlated to CaO/SiO_2.[4] Thus, the calcium oxide equivalent was represented as a combination of the CaO molar equivalents of the deleterious constituents including, SO_3, and MgO as represented in Equation 1.7.[54] Note that in this equation the alkalies were represented independently and not as Na_2O_{eq}.
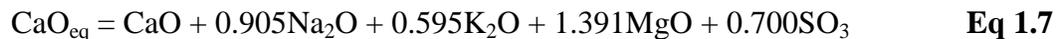
$$CaO_{eq} = CaO + 0.905Na_2O + 0.595K_2O + 1.391MgO + 0.700SO_3 \qquad \textbf{Eq 1.7}$$

With respect to constituents which reduced expansion (SiO_2, Al_2O_3, and Fe_2O_3), SiO_2 was considered the most beneficial in preventing expansion caused by alkali-silica reaction. Therefore, Al_2O_3 and Fe_2O_3 were replaced by their SiO_2 equivalents as shown in Equation 1.8 below.[54]

$$SiO_{2eq} = SiO_2 + 0.589Al_2O_3 + 0.376Fe_2O_3 \qquad \textbf{Eq 1.8}$$
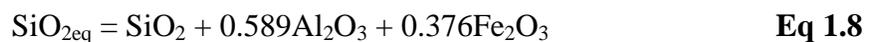
Malvar et al. applied Equations 1.7 and 1.8 to the CaO_{eq}/SiO_{2eq} relationship and compared the ratio with normalized expansion values using the 14-day AMBT method as shown in Figure 1.2.[54]

Figure showing plot with:
$$y = 1.7309x - 0.6879$$
$$R^2 = 0.8287$$
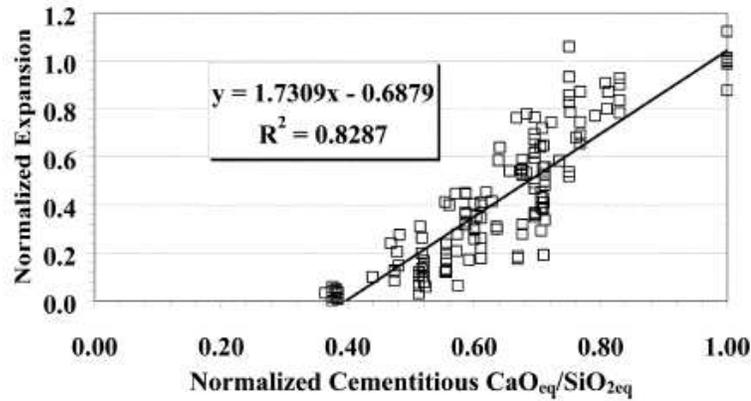
Figure 1.2–Effect of normalized CaOeq/SiO$_2$eq ratio on 14-day AMBT expansion[54]

To account for reactivity of the constituents, Malvar et al. introduced two weighting factors (α and β) in the CaO and SiO_2 equivalencies, which replaced the previous CaO_{eq}/SiO_{2eq} ratio with a chemical index for the blend C_b. This replacement and resulting equation is displayed below.

$$C_b = \frac{CaO_{eq\alpha b}}{SiO_{2eq\beta b}} = \frac{CaO + \alpha\left(0.905Na_2O + 0.595K_2O + 1.391MgO + 0.700SO_3\right)}{SiO_2 + \beta\left(0.589Al_2O_3 + 0.376Fe_2O_3\right)} \qquad \textbf{Eq 1.9}$$

Where α = 5.64 and β = 1.14 are optimal weighting factors as determined by Malvar et al.[54] For a blend of fly ash and cement, the CaO content would be 'W' times the fly ash CaO plus (1-W) times the cement CaO, as represented in Equation 1.10, where W is the weight fraction of the fly ash constituent.[54] The same chemical index can be defined for a blend with no fly ash replacement (0% ash), which is denoted with a C_c in Table 1.7 and Equation 1.11.

$$C_b = \frac{CaO_{eq\alpha b}}{SiO_{2eq\beta b}} = \frac{W\left(CaO_{eq\alpha fa}\right) + (1-W)\left(CaO_{eq\alpha c}\right)}{W\left(SiO_{2eq\beta fa}\right) + (1-W)\left(SiO_{2eq\beta c}\right)} \qquad \textbf{Eq 1.10}$$

$$C_c = \frac{CaO_{eq\alpha c}}{SiO_{2eq\beta c}} = \frac{CaO + 6.0\left(0.905Na_2O + 0.595K_2O + 1.391MgO + 0.700SO_3\right)}{SiO_2 + 1.0\left(0.589Al_2O_3 + 0.376Fe_2O_3\right)} \qquad \textbf{Eq 1.11}$$

Table 1.7. Portland Cement Composition and Chemical Index, Cc[54]

Cement type	Study*	SiO₂	Al₂O₃	Fe₂O₃	CaO	SO₃	MgO	Na₂O_eq	C_c†
High alkali	S&T	20.83	5.11	2.01	62.98	3.25	2.43	1.02	4.17
Low alkali	NM	21.10	4.30	3.20	63.90	3.00	2.00	0.55	3.87
Low alkali	Detwiler	20.87	4.53	2.28	63.99	2.34	3.86	0.43	4.44
High alkali	Touma	20.90	4.43	3.01	62.65	3.06	2.97	1.15	4.32
Medium alkali	Shon	19.12	5.07	3.40	64.73	3.13	0.64	0.65	3.71

*S&T: Shehata and Thomas (2000); NM: McKeen et al. (2000); Detwiler: Detwiler (2003); Touma: Touma et al. (2001); and Shon: Shon et al. (2004).

Table 1.7 displays the various cements Malvar et al used in the study including the chemical constituents used to calculate the chemical index value (C_c). The chemical index can also be defined for a blend with pure fly ash and no cement (100% ash) as denoted by C_{fa} in Table 1.8 and mathematically defined in Equation 1.12.[54]

$$C_{fa} = \frac{CaO_{eq\alpha fa}}{SiO_{2eq\beta fa}} = \frac{CaO + 6.0\left(0.905Na_2O + 0.595K_2O + 1.391MgO + 0.700SO_3\right)}{SiO_2 + 1.0\left(0.589Al_2O_3 + 0.376Fe_2O_3\right)} \qquad \textbf{Eq 1.12}$$

Table 1.8 represents all of the fly ashes studied by Malvar in order of increasing chemical index C_{fa} values. It is noted that a C_{fa} value less than 1.45 typically represents an ASTM C 618 Class F fly ash and a C_{fa} value greater than 1.45 represents a Class C fly ash. These results compare with the Canadian standards and thus the chemical index C_{fa} has a strong correlation with both standards, and particularly strong with the ASTM C 618 sum of ($SiO_2+Al_2O_3+Fe_2O_3$).[54] ASTM C 618, the standard which designates physical and chemical properties of fly ashes and natural pozzolans for use in concrete, requires a Class F fly ash to have a minimum $SiO_2+Al_2O_3+Fe_2O_3$ content of 70% and a minimum of 50% for Class C ashes.[46]

Table 1.8. Fly Ash Type and Chemical Index, Cfa[54]

Fly ash name	Study[*]	Fly ash chemical index C_{fa}[†]	Ash type (ASTM)	Ash type (CSA)	$SiO_2 + Al_2O_3 + Fe_2O_3$[‡]
Escalante (EF)	NM	0.27	F	F	90.9
4-corners (4F)	NM	0.29	F	F	92.3
Coronado (CF)	NM	0.33	F	F	91.0
MN	S&T	0.36	F	CI	86.3
FM	S&T	0.41	F	F	84.8
Low CaO (DL)	Detwiler	0.50	F	F	85.3
LG	S&T	0.52	F	F	81.7
F-Ash (IF)	Touma	0.57	F	CI	80.5
SD II	S&T	0.62	F	CI	79.0
SD I	S&T	0.63	F	CI	79.2
Esc/Tolk (ET)[§]	NM	0.82	F	CI	77.1
C1	S&T	1.21	F	CI	70.5
Medium CaO (DM)	Detwiler	1.32	C	CI	68.5
BD II	S&T	1.40	F	CI	72.6
WM	S&T	1.47	C	CI	66.9
C2	S&T	1.49	C	CH	64.9
PI	S&T	1.54	C	CH	64.6
EW	S&T	1.55	C	CH	62.4
C-Ash (SC)	Shon	1.57	C	CH	62.2
C-Ash (IC)	Touma	1.60	C	CH	61.5
Tolk (TC)	NM	1.63	C	CH	63.4
CC	S&T	1.76	C	CH	58.3
IN	S&T	1.78	C	CH	60.8
TB	S&T	1.83	C	CI	66.4
PP	S&T	1.85	C	CH	60.0
High CaO (DH)	Detwiler	2.00	C	CH	60.0
OK I	S&T	2.07	C	CH	58.2
OK II	S&T	2.43	C	CH	55.6
BR	S&T	2.66	C	CI	57.5

[*]S&T: Shehata and Thomas (2000); NM: McKeen et al. (2000); Detwiler: Detwiler (2003); Touma: Touma et al. (2001); and Shon: Shon et al. (2004).

[‡]Sum of ASTM specified oxides.
[§]50/50 blend of Escalante F (EF) and Tolk C (TC).

Malvar and co-workers determined the amount of fly ash that should be used to produce a mixture with a low risk for ASR based on the chemistry of the fly ash, the reactivity of the aggregate (determined by ASTM C 1260) and the constituents of the particular cement. This was achieved by determining the effect of the C_b/C_c ratio on 14-day AMBT expansion, where the maximum ASTM C 1260 14-day expansion sought was 0.08%. The definition of this ratio incorporated an inverse hyperbolic tangent function as shown in Equation 1.13. Using this equation, the necessary fraction of fly ash to limit expansion to 0.08% with either 50% or 90% reliability was calculated. Equation 1.14 applies the

reliability function and produces the minimum required fly ash replacement (W) as a function of the chemistry of the fly ash ($CaO_{eq\alpha fa}$ and $SiO_{2eq\beta fa}$), the cement chemistry ($CaO_{eq\alpha c}$ and $SiO_{2eq\beta c}$), and the 14-day AMBT expansion with cement only (E_{14c}). This equation can also be used to determine the cement chemical index C_c using Equation 1.11, as well as the fly ash chemical index C_{fa}, setting $W=1$. Once C_{fa} and C_c are determined, and assuming C_c is constant, meaning a single cement is used, W can then be plotted as a function of E_{14c} and C_{fa}, as shown in Figure 1.3. This graph displays the effect of various fly ash replacement levels on the 14-day expansion and compares a range of chemical index C_{fa} values. This graph is based on a C_c value of 4, which is typical for commonly used cements and thus provides a good approximation to find the minimum fly ash replacement for typical cements with 90% reliability that the expansion will be less than the stipulated 0.08%.[54]

$$\frac{C_b}{C_c}=g\left(\frac{0.08}{E_{14c}}\right)=a_4\tanh^{-1}\left(\frac{2\left(0.08/E_{14c}\right)-\left(a_1+a_2\right)}{a_2-a_1}\right)+a_3 \qquad \textbf{Eq 1.13}$$

$$W=\frac{1-g\left(0.08/E_{14c}\right)}{\left(1-\frac{CaO_{eq\alpha fa}}{CaO_{eq\alpha c}}\right)-\left(1-\frac{SiO_{2eq\beta fa}}{SiO_{2eq\beta c}}\right)g\left(0.08/E_{14c}\right)} \qquad \textbf{Eq 1.14}$$
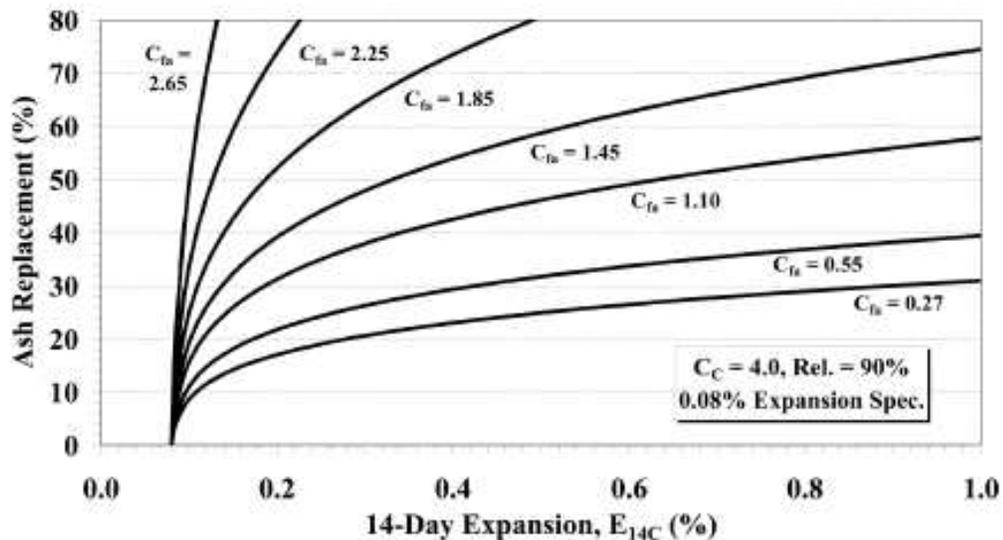
Figure 1.3–Minimum fly ash replacement to mitigate alkali-silica reaction with 90% reliability[54]

However, their work also suggested that a 50% reliability may provide the "best guess" and was found to be more in line with results of experimental work. This is shown below in Figure 1.4.
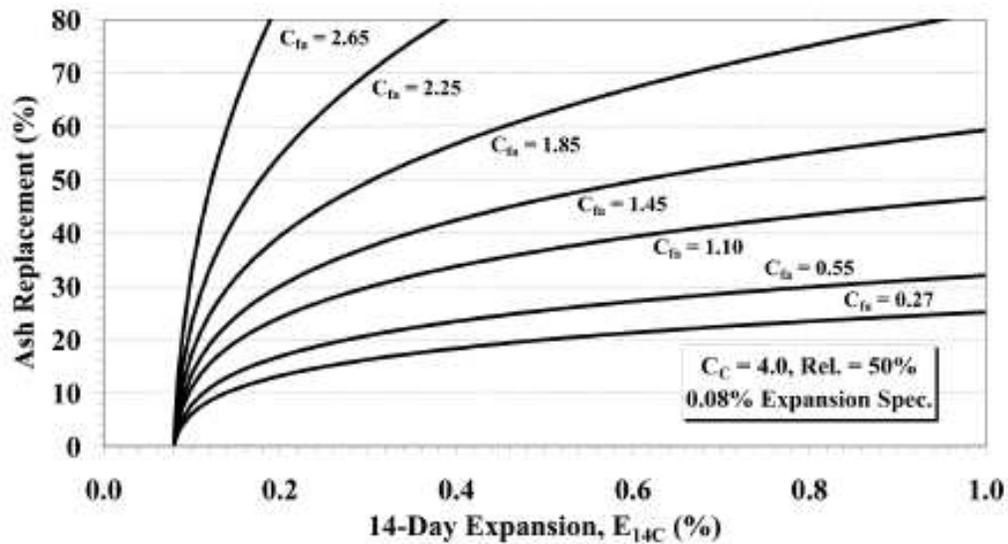
Figure 1.4–Minimum fly ash replacement to mitigate alkali-silica reaction with 50% reliability[54]

Malvar and co-worker's fly ash chemical index C_{fa} has strong correlation with ASTM C 618 as well as the related Canadian Standards.[54] However, ASTM C 618 does not include any requirements regarding the limits of available alkalies from fly ash. Values reported in work by Malvar and co-workers were obtained from their referenced sources.[59] Thus, it is necessary to establish a rapid test method to confidently determine the alkali contribution from the fly ash, which could then be implemented into this index. Determining the true alkali contribution from fly ash and incorporating that value into the chemical index would provide reliable information for the calculation of the minimum fly ash replacement level to successfully mitigate expansion due to alkali-silica reaction.

1.2.10 Sustainability

Concrete is an environmentally sound building material as concrete roads and buildings last longer and require less maintenance than other building materials.[66]   When concrete is used as the material for freeways, less consumption of vehicle fuel can result.[66]   Also, recent studies have 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.[49]   Concrete can be made more sustainable, however, with the use of supplementary cementing materials. Replacing portions of portland cement with fly ash assists in reducing the depletion of natural resources (otherwise used for portland cement production) and significantly decreases the energy-intensive manufacturing of portland cement. Thus, savings in both energy usage as well as greenhouse gas emissions result from the use of fly ash 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.[49]

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.[49] 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 (CCPs) has increased by 450%. However, in that same period there has only been an increase in use of that material from 18% in 1966 to just over 40% in 2007.[45] Certainly there exists a great deal of material that is currently land filled that could be potentially reclaimed for use in a wide variety of applications.

Supplementing portland cement with fly ash 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.

1.3   References

1.   Ideker, J., *Crack in concrete slab caused by Alkali-Silica Reaction*, K. Schwing, Editor. 2009: Corvallis.
2.   Kurtis, K., *Portland Cement Hydration*. 2007, School of Civil Engineering, Georgia Institute of Technology: Atlanta, Georgia. p. 35.
3.   Stanton, T.E., *Expansion of Concrete Through Reaction Between Cement and Aggregate*. American Society of Civil Engineers, 1940. **66**: p. 1781-1811.
4.   Folliard, K.J., et al., *Interim Recommendations for the Use of Lithium to Mitigate or Prevent Alkali-Silica Reaction (ASR)*. July 2006, Federal Highway Administration.
5.   Mehta, P.K. and P.J.M. Monteiro, *Concrete: Microstructure, Properties, and Materials*. 3 ed. 2006, New York: McGraw-Hill.
6.   Pedneault, A., *Development of Testing and Analytical Procedures for teh Evaluation of the Residual Potential of Reaction, Expansion, and Deterioration of Concrete Affected by ASR*. 1996, Laval University: Quebec City, Canada. p. 133.
7.   Thomas, M.D.A., *The role of calcium in alkali-silica reaction.* Materials Science of Concrete - The Sidney Diamond Symposium, 2002: p. 325-331.
8.   Hansen, W.C., *Studies Relating to the Mechanism by Which the Alkali-Silica Reaction Proceeds in Concrete.* Journal of the American Concrete Institute, 1944. **15**(3): p. 213-27.
9.   Wang, H. and J.E. Gillott, *Mechanism of Alkali-Silica Reaction and the Significance of Calcium Hydroxide*. Cement and Concrete Research, 1991. **21**(4): p. 647-654.
10.   Chatterji, S., *The Role of Ca(OH)$_2$ in the Breakdown of Portland Cement Concrete due to Alkali-Silica Reaction.* Cement and Concrete Research, 1979. **9**(2): p. 185-188.
11.   Chatterji, S. and N.F. Clausson-Kass, *Prevention of Alkali-Silica Expansion by Using Slag-Portland Cement.* Cement and Concrete Research, 1984. **14**(6): p. 816-818.
12.   Diamond, S. *ASR −Another Look at Mechanisms*. in *Proceedings of the 8th International Conference on Alkali-Aggregate Reaction*. 1989. Kyoto.
13.   Thomas, M.D.A., P.J. Nixon, and K. Pettifer. *Effect of Pulverised-Fuel Ash With a High Total Alkali Content on Alkali Silica Reaction in Concrete Containing Natural UK Aggregate*. in *Proceedings of the 2nd CANMET/ACI International Conference on Durability of Concrete* 1991. Detroit: American Concrete Institute.
14.   Bleszynski, R.F. and M.D.A. Thomas, *Microstructural Studies of Alkali-silica Reaction in Fly Ash Concrete Immersed in Alkaline Solutions.* Advanced Cement Based Materials, 1998. **7**: p. 66-78.
15.   Hansen, W.C., *Studies Relating to the Mechanism by Which the Alkali-Silica Reaction Proceeds in Concrete.* Journal of the American Concrete Institute, 1944. **15**: p. 213-227.
16.   Chatterji, S., Thalow, N., Jensen, A.D., *Studies of the Alkali-Silica Reaction, Part 4: Effect of Different Alkali Salt Solutions on Expansion.* Cement and Concrete Research, 1987. **17**: p. 777-783.
17.   Rotter, H.M., *Alkali-aggregateReaction: From Basic Principles to Structural Behavior - Literature Review*. 1995, Department of Civil Engineering, École Polytechnique de Montréal: Montréal, PQ.
18.   Prezzi, M., P.J.M. Monteiro, and G. Sposito, *The Alkali-Silica Reaction, Part I: Use of the Double-Layer Theory to Explain the Behavior of Reaction-Product Gels.* ACI Materials Journal, 1997. **January-February 1997**(Title no.94-M2): p. 10-17.

19. *Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)*, in *ASTM C 1260*. 2007, ASTM International: West Conshohocken, PA. p. 5.

20. Thomas, M.D.A., et al., *Performance Limits for Evaluating Supplementary Cementing Materials using the Accelerated Mortar Bar Test.* PCA R&D Serial No. 2892, 2005: p. 1-22.

21. *Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)*, in *ASTM C 1567*. 2008, ASTM International: West Conshohocken, PA. p. 6.

22. Leemann, A., B. Lothenbach, and C. Thalmann, *Influence of superplasticizers on pore solution composition and on expansion of concrete due to alkali-silica reaction.* Construction and Building Materials, 2011. **25**(1): p. 344-350.

23. *Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction*, in *ASTM C 1293-08b*, A. International, Editor. 2008, ASTM International: West Conshohocken, PA. p. 7.

24. *Standard Practice for Laboratory Testing to Demonstrate the Effectiveness of Supplementary Cementing Materials and Lithium-based Admixtures to Prevent Alkali-silica Reaction in Concrete*, in *A23.2-28A*. 2004b, Canadian Standards Association: Mississauga, ON, CA. p. 327-330.

25. *Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction*, in *ASTM C 1293-08*. 2008, ASTM International: West Conshohocken, PA. p. 6.

26. *Standard Practice for Petrographic Examination of Hardened Concrete*, in *ASTM C856-04*, ASTM, Editor. 2004, ASTM International: West Conshohocken, Pa. p. 17.

27. Guthrie, G.D. and J.W. Carey, *Geochemical Methods for the Identification of ASR Gel.* 1998, Los Alamos National Laboratory: Los Alamos, NM. p. 13.

28. USACE, *Unified Facilities Guide Specifications*, in *UFGS-32 13 11*, USACE, Editor. 2007.

29. Malvar, L.J., *ASR guidelines in DOD Unified Facilities Guide Specifications.* 2009, NAVFAC ESC: Port Hueneme, CA.

30. Tremblay, C., et al., *Experimental investigation of the mechanisms by which LiNO3 is effective against ASR.* Cement and Concrete Research, 2010. **40**(4): p. 583-597.

31. Tremblay, C., et al., *Effectiveness of Lithium-Based Products in Concrete Made with Canadian Natural Aggregates Susceptible to Alkali- Silica Reactivity.* ACI Materials Journal, 2007. **104**(2): p. 195-205.

32. Stark, D. *Lithium Salt Admixtures - An Alternative Method to Prevent Expansive Alkali-Silica Reactivity*. in *Ninth International Conference on Alkali-Aggregate Reaction in Concrete*. 1992. London, United Kingdom.

33. Barborak, R., *Using Lithium Compounds as an Admixture in New Concrete and as a Posttreatment for Exisiting Concrete Affected by Alkali-silica Reaction*, in *Department of Civil, Architectural and Environmental Engineering*. 2005, The University of Texas at Austin: Austin, Texas.

34. Kosmatka, S.H., B. Kerkhoff, and W.C. Panarese, *Design and Control of Concrete Mixtures*. 14 ed. 2008, Skokie, Illinois: Portland Cement Association.

35. Mehta, P.K. and K.J. Folliard. *Rice Husk Ash-A Unique Supplementary Cementing Material*. in *Proceedings of teh International Symposium on Advances in Concrete Technology*. 1992.

36. Siddique, R. and J. Klaus, *Influence of metakaolin on the properties of mortar and concrete: A review.* Applied Clay Science, 2009. **43**(3-4): p. 392-400.

37.   Zhang, M.H., R. Lastra, and V.M. Malhotra, *Rice-husk ash paste and concrete: Some aspects of hydration and the microstructure of the interfacial zone between the aggregate and paste.* Cement and Concrete Research, 1996. **26**(6): p. 963-977.

38.   Dong, D.V., P.D. Huu, and N.N. Lan. *Effect of Rice Husk Ash on Properties of High Strength Concrete*. in *The 3rd ACF International Conference - ACF/VCA 2008*. 2008.

39.   Ramezanianpour, A.A., K. Zarrabi, and M. Mahdikhani, *Mitigation of Alkali Aggregate Reaction of Concrete Incorporation Rice Husk Ash (RHA)*, Department of Civil Engineering, Amirkabir University of Technology: Tehran, Iran.

40.   Multon, S., et al., *Effects of aggregate size and alkali content on ASR expansion.* Cement and Concrete Research, 2010. **40**(4): p. 508-516.

41.   318, A.C., *Structural Building Code*, in *ACI Committee 318, ACI 318*, ACI, Editor. 2008, ACI: Farmington Hills, Michigan.

42.   Thomas, M.D.A., *Optimizing the Use of Fly Ash in Concrete*. 2007, PCA: Skokie, Illinois. p. 24.

43.   Daderko, G., *Concrete Failures...and How SCMs Can Help Prevent Them.* The Construction Specifier, 2008: p. 26-38.

44.   Mehta, P.K. and P.J.M. Monteiro, *Concrete: Microstructure, Properties, and Materials*. 3 ed. 2006, New York: McGraw-Hill. 659.

45.   Association, A.C.A. *Advancing the Management and use of Coal Combustion Products*. 2009 [cited 2009 May 7]; Available from: http://www.acaa-usa.org/.

46.   *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, in *ASTM C 618*, A. International, Editor. 2008, ASTM International: West Conshocken, Pennsylvania. p. 3.

47.   Shehata, M.H. and M.D.A. Thomas, *Alkali Release Characteristics of Blended Cements.* Cement and Concrete Research, 2006. **36**(6): p. 1166-1175.

48.   Glasser, F.P., ed. *Chemistry of the Alkali-Aggregate Reaction*. The Alkali-Silica Reaction in Concrete, ed. R.N. Swamy. 1992: Blackie, London, United Kingdom. 96-121.

49.   Headwaters, *Fly Ash for Concrete*, H. Resources, Editor. 2005: South Jordan, Utah.

50.   Mehta, K.P. *High-Performance, High-Volume Fly Ash Concrete for Sustainable Development*. in *International Workshop on Sustainable Development and Concrete Technology*. 2004. Beijing, China.

51.   Duchesne, J. and M.A. Be´rube´, *Effect of supplementary cementing materials on the composition of cement hydration products.* Advanced Cement Based Materials, 1995. **2**(2): p. 43-52.

52.   Shehata, M.H., M.D.A. Thomas, and R.F. Bleszynski, *The Effects of Fly Ash Composition on the Chemistry of Pore Solution in Hydrated Cement Pastes.* Cement and Concrete Research, 1999. **29**: p. 1915-1920.

53.   Diamond, S., *Effects of two Danish fly ashes on alkali contents of pore solutions of cement fly ash pastes.* Cement and Concrete Research, 1981. **11**(3): p. 383-94.

54.   Malvar, L.J. and L.R. Lenke, *Efficiency of Fly Ash in Mitigating Alkali-Silica Reaction Based on Chemical Composition.* ACI Materials Journal, 2006. **103**(5): p. 319-326.

55.   AACA, *Fly Ash Facts for Highway Engineers*, in *Federal Highway Administration Report FHWA-SA-94-081*. 1995, American Coal Ash Association: Washington, D.C. p. 70.

56.   NMDOT, *Supplement to the 2000 Edition of the Standard Specifications for Highway and Bridge Construction*, N.M.D.o. Transportation, Editor. 2004.

57.   Malvar, L.J., et al., *Closure to Discussion of "Alkali Silica Reaction Mitigation: State-of-the-Art and Recommendations".* ACI Materials Journal, 2003. **100**(4): p. 346-350.

58. Mehta, P.K. *Standard Specifications for Mineral Admixtures - An Overview*. in *Proceedings of Second CANMET/ACI International Conference*. 1986. Farmington Hills, Mich.

59. *ASTM C618 Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, in *ASTM C618-09*, A. International, Editor. 2009, ASTM International: West Conshohocken, PA.

60. Klieger, P. and S. Gebler. *Fly Ash and Concrete Durability*. in *Concrete Durability: Katharine and Bryant Mather International Conference*. 1987. Farmington Hills, Mich: American Concrete Institute.

61. Malhotra, V.M. and A.A. Ramezanianpour, *Fly Ash in Concrete*, in *Canada Center for Mineral and Energy Technology, Natural Resources Canada,* , CANMET, Editor. 1994, MSL 94-45(IR): Ottawa, Ontario, Canada. p. 307.

62. Shehata, M.H. and M.D.A. Thomas, *Alkali release characteristics of blended cements.* Cement and Concrete Research, 2006. **36**: p. 1166-1175.

63. Thomas, M. and M. Shehata, *Use of Blended Cements to Control Expansion of Concrete due to Alkali-Silica Reaction*, in *Eighth CANMET/ACI International Conference on Flyash, Silica Fume, Slag And Natural Pozzolans in Concrete*, P. Gupta, Editor. 2004: Las Vegas, U.S.A. p. 591-607.

64. ASTM, *Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete*, in *ASTM C311*. 2007, ASTM International: West Conshohocken, PA.

65. Thomas, M., et al., *Test methods for evaluating preventive measures for controlling expansion due to alkali-silica reaction in concrete.* Cement and Concrete Research, 2006. **36**: p. 1842-1856.

66. Headwaters. *Fly Ash and the Environment*. 2010 [cited 2010 October 20, 2010]; Available from: http://www.flyash.com/flyashenvironment.asp.

Influence of Alkalies from Fly Ash to Pore Solution: ASR Consideration

Kelsea A. Schwing, Jason H. Ideker, Kevin J. Folliard, Michael D.A. Thomas

2   First Manuscript

Influence of Alkalies from Fly Ash to Pore Solution: ASR Consideration

Kelsea Schwing[1], Jason H. Ideker[2], and Kevin J. Folliard[3], Michael D.A. Thomas[4]

Abstract: An ongoing debate in the concrete durability community is the availability of alkalies from fly ash to concrete pore solution. As part of a project to develop a rapid test method to determine the "true" alkali contribution from fly ash the authors first performed a series of ASTM C 1567 tests. Results confirmed that lower-alkali fly ashes (of similar CaO content) better mitigated expansion due to ASR but the test could not accurately capture the influence of alkalies from the fly ash. A chemical index characterization technique, by Malvar et al., was applied to calculate the required fly ash replacement quantity based on the raw fly ash chemistry and 14-day AMBT results without fly ash. The chemical index proved promising for low-alkali fly ashes; however, adjustments are necessary to include borderline and high-alkali fly ashes. Development of a rapid test method to accurately determine the alkali contribution from fly ash will enable more fly ashes to be effectively used to produce durable concrete in the field.

Keywords: Alkali-Silica Reaction, Fly Ash, Alkali Availability.

---

[1] Graduate Research Assistant, School of Civil and Construction Engineering, Oregon State University, USA; E-mail: kelsea2122@gmail.com

[2] Assistant Professor, School of Civil and Construction Engineering, Oregon State University, USA; E-mail: jason.ideker@oregonstate.edu

[3] Associate Professor, Department of Civil, Architectural, and Environmental Engineering, The University of Texas at Austin, USA; E-mail: folliard@mail.utexas.edu

[4] Professor, University of New Brunswick, NB; E-mail: mdat@unb.ca

2.1   Introduction

2.1.1   Alkali-Silica Reaction

Alkali-silica reaction (ASR) is one of the leading causes of concrete deterioration worldwide, second only to the corrosion of reinforcing steel. ASR occurs internally in concrete between the alkalies (Na^+ and K^+), hydroxyl ions (OH^-) of the cementitious material and reactive silica in certain aggregates. Three conditions are necessary for ASR gel to be formed: (1) available alkalies in pore solution; (2) reactive silica present in the aggregates; and (3) sufficient moisture available to drive the reaction. When all three of these conditions are met, a gel-like material, rich in alkalies, silica and other ions is formed in and around aggregates as well as within the pores of the concrete. This gel has a high affinity to absorb water molecules both contributed from the pore solution as well as from external sources. The gel expands with the absorption of water, exerting tensile forces within the concrete matrix which can result in cracking when the forces exceed the tensile capacity of the concrete. Once cracking occurs, external water can more easily penetrate the concrete, thereby exacerbating ASR and increasing the potential for other durability mechanisms, such as corrosion, sulfate or freeze-thaw attack to further deteriorate the concrete.

Eliminating any of the three conditions necessary for ASR (sufficient alkalies, reactive silica provided by the aggregates, and available moisture) may effectively minimize or even eliminate expansion due to alkali silica reaction. However, it may be challenging and in fact impossible to eliminate all or even any of these conditions and doing so may induce other detrimental factors for the concrete. As a result, much attention has been focused in the past 70 years on mitigation strategies to eliminate or at the very least, reduce the risk of deleterious ASR. Typical mitigation strategies involve the use of supplementary cementing materials (SCMs), such as fly ash, silica fume, ground granulated blast furnace slag, metakaolin, rice husk ash and other natural pozzolans. To a lesser extent, chemical admixtures, mainly lithium-based salts, have also been used effectively to limit ASR in new concrete.

2.1.2   Fly Ash and the mitigation of ASR

Of particular interest is the use of fly ash as an SCM as it improves the workability of fresh concrete as well as increases the strength and long-term performance of hardened concrete and would otherwise be landfilled. Additionally, it has been understood for over 60 years that fly ash can effectively mitigate expansion due to ASR. A byproduct of the coal-burning industry, fly ash consists of finely divided uncombusted mineral impurities which are fused together and solidify upon cooling as the combustion gases are transported from the combustion chamber. The efficiency of fly ash in controlling the alkali silica reaction depends on several parameters including:[1]

- Dosage of fly ash (typically expressed as a mass replacement of cement)
- Chemical composition of the fly ash (of particular importance are the lime (CaO) content and alkali content of the ash).
- Reactivity of the aggregate
- Chemical composition of the concrete (in particular the alkali content or "loading")

The chemical composition of the fly ash is primarily dependent on the source of the coal burned in the power plant. With respect to ASR mitigation, the primary constituents of interest are the calcium oxide (CaO) and the alkali (Na^+ and K^+) contents of the fly ash. Typically, as the amount of CaO increases, the efficiency of controlling ASR (at a constant replacement percentage) decreases. In general, low-calcium (Class F, less than 10% CaO) ashes are more effective in controlling ASR than high calcium ashes (Class C, 10% to 30% CaO), primarily due to a higher alkali-binding capacity.[2, 3] Low calcium fly ashes contain a higher silica concentration than high calcium ashes, leading to production of a C-S-H structure with lower calcium to silica ratio. The resulting C-S-H has a higher affinity for cations, namely alkalies, which are absorbed from the pore solution.[1, 3, 4] In addition, low calcium ashes are more efficient in controlling expansion due to ASR because the alkalies provided by the ash are not readily available for reaction, whereas the alkalies contained in high-calcium ashes tend to be more readily

available to the pore solution.[1, 5] As a result, higher dosages of high calcium fly ashes are needed to mitigate expansion due to ASR.[1]

The alkalies in the pore solution have been shown to be directly correlated to the alkali, calcium, and silica content of the cementing materials. Additionally, hydroxyl ions (OH$^-$) are prevalent in the pore solution at roughly the same concentration as the alkali ions so as to maintain chemical equilibrium.[6, 7] A mathematical relationship has thus been derived by Thomas et al. to determine the OH$^-$ or (Na$^+$ + K$^+$) concentration of the pore solution depending on the chemical composition of the cementitious blend. This relationship is expressed by Equation 2.1[8]:

$$OH^- = 6 \text{ x } (Na_2O_{eq} * CaO)/(SiO_2)^2 \qquad \textbf{Eq. 2.1}$$

Where,

$$Na_2O_{eq} = Na_2O + 0.658 \text{ x } K_2O \qquad \textbf{Eq. 2.2}$$

Na_2O_{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 alkalies (Na$^+$ + K$^+$) are represented by Na$_2$O$_{eq}$, as presented by Equation 2.2[1], which denotes the quantity of alkalies in the material. 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, alkalies from the hydrates are released to maintain equilibrium between the solid and liquid phases.[9] As the Na$_2$O$_e$ of the fly ash increases, so does the amount of alkalies that may be released from the ash to the pore solution, thus resulting in a pore solution of higher alkalinity. Both CaO and SiO$_2$ affect the amount of silica and calcium in the system consequently 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 alkalies from the pore solution and therefore a lower alkalinity of the pore solution.[3]

Despite significant research efforts, many fly ashes are sometimes restricted from use because of insufficient test methods to accurately determine their chemical compositions. One reason for avoiding the use of a certain fly ash in concrete is its available alkali content, which although not currently prescriptively specified in ASTM C 618, falls under scrutiny due to concerns regarding ASR potential as a result of alkali contribution from the ash to the concrete pore solution. Because there is very little guidance and no standardized test to measure the "true" contribution of alkalies from a given ash in a real concrete mixture, many ashes are simply avoided, particularly those falling in the "borderline" category (ashes that may be precluded from use in the field due to their chemical composition).

2.1.3   Test procedure for determining the effectiveness of fly ash to mitigate ASR

A variety of test methods to detect alkali-silica reactivity have been developed over the past 70 years. Most recently several of these test methods have been modified to allow for testing the efficiency of mitigation options including supplementary cement materials and/or chemical admixtures. However, the more reliable test methods for assessing performance of fly ash in controlling ASR, such as the concrete prism test (ASTM C 1293) have not been widely accepted for use in the field due to extended time requirements. As a result, rapid test methods, such as the 16-day ASTM C 1567 are of high demand; however the effectiveness of these test methods for assessing nuances such as influence of alkali content or environmental factors are questionable at best.

ASTM C 1567, also referred to as the accelerated mortar bar test (AMBT), (the standard test method for determining the potential alkali-silica reactivity of combinations of cementitious materials and aggregate), has proven to be a functional method for determining the effectiveness of fly ash to mitigate expansion due to alkali-silica reaction.[10] ASTM C 1567 and ASTM C 1260 follow the same testing procedure with the inclusion of supplementary cementing materials in ASTM C 1567 instead of a strictly cement mortar as in ASTM C 1260. To avoid confusion, all reference to this test in this document will be labeled as ASTM C 1567. The test involves casting mortar prisms that

measure 1 in. x 1 in. x 11.25 in (25 mm x 25 mm x 285 mm). A stainless steel gage stud is cast into both ends of each bar to provide an effective gage length of 10.00 ± 0.10 in. (250 ± 2.5 mm). After curing for 24 ± 2h in a 100% relative humidity room at 73.4 ± 3 °F (23 ± 1.7 °C), the specimens are measured and submerged in tap water, then 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 ± 2h later and the bars are quickly transferred to a solution of 1 N NaOH which is already at 176 ± 3.6 °F (80.0 ± 2.0 °C). The bars then remain in 1 N NaOH at 176 ± 3.6 °F (80.0 ± 2.0 °C) for a period of 14 days. Some researchers extend this exposure period to 28 days. Periodic length measurements are taken throughout this time period at approximately the same time each day. Length change is recorded to the nearest 0.0001 inch and results are presented for the average of three or four mortar bars to the nearest 0.01%.[11]

Expansion criteria for this test fall into three categories within ASTM C 1567 based on expansion occurring 16 days after casting (14 days after immersion in 1 N NaOH). Expansions of less than 0.10% are generally considered to be indicative of innocuous behavior. Expansions of more than 0.20% indicate that the materials are potentially deleterious. Expansions that fall between 0.10 and 0.20% indicate that the aggregate may exhibit either innocuous or deleterious performance in the field.[11] The above expansion criteria, as described in the non-mandatory appendix of ASTM C 1567, are not actually used by many researchers or agencies, but rather, the consensus among many ASR researchers and engineers is a single expansion limit of 0.10% after 14 days of immersion in the soak solution.[12] However, other agencies may use stricter limits such as lower expansion limits combined with longer exposure periods to 1 N NaOH. This may be especially useful for critical structures where little expansion can be accommodated or tolerated (e.g. airfield pavements, dams and concrete structures with internal mechanical features).

2.1.4   Chemical Index

Recent research by Malvar and co-workers [13] has shown promise in predicting the efficacy of fly ash to control alkali-silica reaction utilizing the accelerated mortar bar test method (AMBT). These authors developed a chemical index using the characteristics of a particular fly ash and cement combination which could then be utilized to predict the effectiveness of that material in controlling deleterious ASR in the accelerated mortar bar test. An expansion limit of 0.08% was decided based on a report published by Committee 221 of the American Concrete Institute (ACI) specifying this value as the limit for ASTM C 1260.[13-15]   Malvar et al. showed that the 14-day expansion in the AMBT would remain below 0.08%, with either 50% reliability (for best prediction) or 90% reliability (for safety due to a "built-in" safety factor correlated to the fly ash constituents), for a minimum cement replacement level (replacement with fly ash) determined with this chemical index. A minimum required fly ash substitution level could be determined with three different sets of inputs based on the cement chemistry, the fly ash chemistry and the 14-day AMBT results with cement only (e.g. aggregate reactivity level).[13]

2.2   Research significance

The purpose of this study was to determine the effectiveness of fly ash to mitigate alkali silica reaction using the accelerated mortar bar test with particular focus on the chemical composition of the fly ash. The two primary constituents of interest were the alkali (Na^+ and K^+) and calcium oxide (CaO) concentrations. The relationship between these concentrations and the ability of fly ash to mitigate ASR expansion in the accelerated mortar bar test was analyzed and discussed. Results of the AMBT were applied to the chemical index proposed by Malvar et al. to determine the effectiveness of the index with fly ashes of varying chemical constituents. This information will aide in the development of a rapid test method to determine the "true" alkali contribution from fly ash to the pore solution of concrete by providing a solid mathematical and experimental approach which will be applied to current laboratory and analytical testing.

2.3   Procedure

The procedures outlined by the ASTM C 1567-08 standard were followed and all sodium hydroxide solutions were titrated to ensure proper normality ($\pm$ 0.01 N).[16]   Although ASTM C 1567 calls for a duration of 14 days exposure to 1 N NaOH, it was decided to run tests for a period of 28 days to evaluate the trends beyond the 2 week period. Length measurements were taken at 0, 1, 4, 7, 10, 12, 14, 18, 21, 25, and 28 days for all tests. Typical fly ash replacement levels range from 15-50% by mass, thus replacements of 25%, 35% and 45% were compared against tests run with 0% fly ash replacement.[2]

2.4   Materials

The materials for this project were chosen carefully to ensure a wide range of chemical constituents. The cement used was an ASTM C 150 Type I cement with a high alkali content. Constituents of the cement used in the study are presented in Table 2.1. The fly ashes used included those which have already shown promise for mitigating ASR, ashes which are considered borderline ashes, as well as those that are considered to be ineffective in controlling ASR at standard dosage rates (e.g. 15-40%). The fly ashes used in the study were carefully chosen to represent a broad spectrum of alkali and calcium contents. The full realm of chemical constituents of all fly ashes tested is also provided in Table 2.1.

Table 2.1: Fly ash and Portland cement composition

Constituent (Wt%, dry basis)	FA1	FA2	FA3	FA4	FA5	Cement
SiO_2	47.66	33.16	54.06	63.95	59.36	20.08
Al_2O_3	21.58	17.04	16.36	16.54	25.14	5.61
Fe_2O_3	4.21	4.91	6.01	4.43	5.56	2.51
$SiO_2+Al_2O_3+Fe_2O_3$	73.45	55.11	76.42	84.92	90.06	0.79
CaO	12.3	27.06	11.16	6.16	5.63	63.79
MgO	2.7	5.06	4.14	2.38	0.94	1.22
Na_2O	6.02	5.09	3.3	2.31	0.40	0.13
K_2O	0.89	0.78	1.86	1.47	0.97	1.0
TiO_2	0.97	1.11	0.98	0.9	1.09	0.24
MnO_2	0.02	0.05	0.1	0.05	0.08	0.05
P_2O_5	0.47	0.51	0.29	0.3	0.03	0.29
SrO	0.42	0.61	0.32	0.21	0.11	0.09
BaO	0.8	1.17	0.55	0.46	0.16	0.02
SO_3	1.2	2.87	0.64	0.54	0.37	3.39
LOI	0.76	0.58	0.24	0.31	0.16	1.59
Moisture, as received	0.09	0.15	0.06	0.04	0.04	
Na_2O^a	1.93	4.2	1.18	0.95	0.15	
K_2O^a	0.29	0.54	0.56	0.52	0.31	
Na_2O^b	6.61	5.60	4.52	3.28	1.04	0.79
C_3S						56.2
C_3A						10.61
C_2S						15.17
C_4AF						7.64

[a] Available alkali, as per ASTM C311
[b] Total alkali ($Na_2O+0.658K_2O$)

Three fine aggregates were used in the ASTM C 1567 accelerated mortar bar tests which are presented in Table 2.2. These aggregates were chosen to account for both high and moderate reactivity as well as to include aggregates with various petrographic compositions. After conducting a series of tests it was decided that Aggregate 3 and Aggregate 1 had very similar reactive properties and thus it was decided to discontinue testing with Aggregate 3.

Table 2.2: Fine Aggregates Used in Accelerated Mortar Bar Testing

Aggregate	Source	Reactivity Level ASTM C 1567)	Petrographic Description
A1	Oregon	High	Natural sand, mixed volcanic
A2	Texas	Moderate	Mixed quartz/chert sand
A3	Texas	High	Mixed quartz/chert/feldspar sand

2.5   Results and Discussion

2.5.1   Expansion

In this project, 39 different ASTM C 1567 (AMBT) tests were performed. These consisted of a variety of mixtures of three reactive fine aggregates combined with five different fly ashes and a high alkali ASTM C 150 Type I cement. Four samples of each mixture combination were cast and the average of the expansions results, both 14 day and 28 day, are tabulated in Table 2.3.

Table 2.3 – 14-day and 28-day AMBT Expansion Results reported to the nearest 0.001%

Fly Ash	Mix	14-day expansions (%)	28-day expansions (%)
No Fly Ash	A1	0.656	0.8513
	A1 test 2	0.602	0.8128
	A2	0.2797	0.4053
	A3	0.7713	0.9105
	A3 test 2	0.7058	0.8565
Fly Ash 1	A1 + 25% FA1	0.0845	0.2103
	A1 + 35% FA1	0.0223	0.1020
	A1 + 45% FA1	0.0073	0.0573
	A2 + 25% FA1	0.0787	0.1382
	A2 + 35% FA1	0.0210	0.0457
	A2 + 45% FA1	0.0102	0.0627
Fly Ash 2	A1 + 25% FA2	0.4900	0.6585
	A1 + 35% FA2	0.1890	0.3548
	A1 + 45% FA2	0.143	0.2730
	A2 + 25% FA2	0.3297	0.4073
	A2 + 35% FA2	0.1503	0.2103
	A2 + 45% FA2	0.1053	0.1977
	A3 + 25% FA2	0.5998	0.6993
	A3 + 35% FA2	0.4067	0.5193
	A3 + 45% FA2	0.3763	0.4940
Fly Ash 3	A1 + 25% FA3	0.1598	0.3087
	A1 + 35% FA3	0.0393	0.1423
	A1 + 45% FA3	0.0263	0.1153
	A2 + 25% FA3	0.1370	0.2345
	A2 + 35% FA3	0.0360	0.0955
	A2 + 45% FA3	0.0120	0.0540
Fly Ash 4	A1 + 25% FA4	0.1105	0.2780
	A1 + 35% FA4	0.0533	0.1543
	A1 + 45% FA4	0.0310	0.0865
	A2 + 25% FA4	0.0365	0.1160
	A2 + 35% FA4	0.0308	0.0442
	A2 + 45% FA4	0.0395	0.0550

	A1 + 25% FA5	0.0295	0.1207
	A1 + 35% FA5	0.0203	0.0570
	A1 + 45% FA5	0.0130	0.0400
Fly Ash 5	A2 + 25% FA5	0.0403	0.0862
	A2 + 35% FA5	0.0178	0.0522
	A2 + 45% FA5	0.0110	0.0332

Expansion results for Aggregate 1 with FA2 and FA5 are shown in Figure 2.1 below. These fly ashes were represented due to their differing alkali (FA2: 5.60% and FA5: 1.04%) and CaO constituents (FA2: 27.06% and FA5: 5.63%). Each test was carried out for 28 days, however the vertical line represents the 14-day measurement. The two horizontal lines, at 0.1% and 0.2% expansion indicate the limits stated by the standard, as discussed previously.
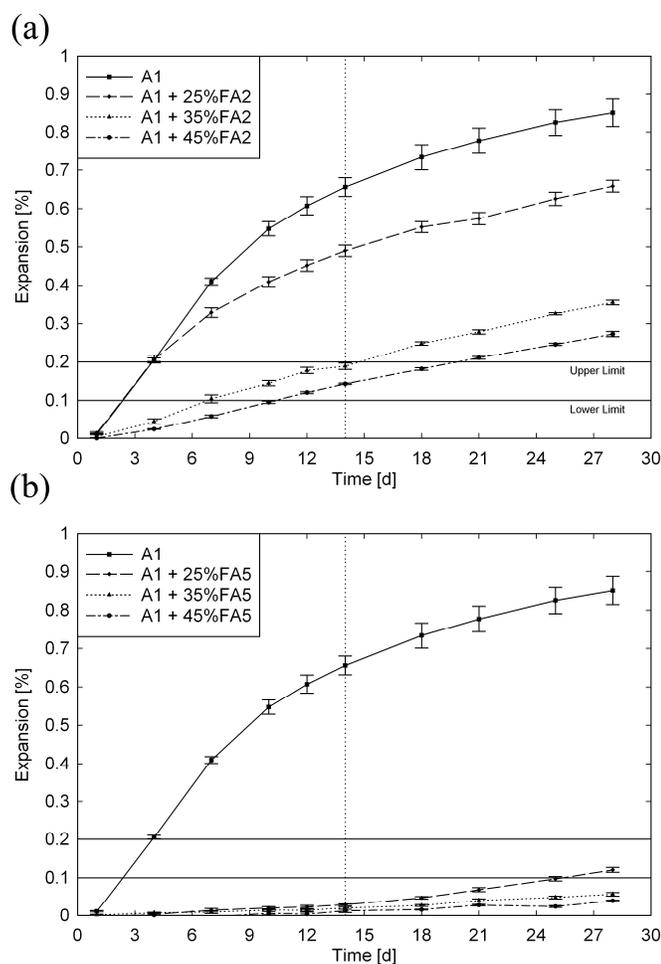
Figure 2.1 – Aggregate 1 with 0%, 25%, 35% and 45% replacement levels of a) FA1 and b) FA5

It is clear from these graphs that increasing the level of fly ash replacement decreases the expansion due to alkali silica reaction for all fly ashes studied when mixed with Aggregate 1. Furthermore, FA2, which is a high alkali, high calcium oxide fly ash, was not as effective in mitigating ASR as any of the other lower alkali, lower CaO fly ashes, particularly FA5. These results suggest that either the higher CaO content or the higher total alkali content (or both) of FA2 decreases the ash's ability to mitigate ASR. The best way to evaluate the influence of the role of alkalies on ASR-related expansion is through more reliable ASTM C 1293 testing or outdoor exposure blocks where the pore solution is not overwhelmed by 1 N NaOH as in the ASTM C 1567 test. However, it is interesting to observe that a clear trend can be seen for ashes with higher alkali contents compared to those with lower concentrations. Significantly higher replacement levels of FA2 would be necessary to control deleterious ASR with this highly reactive fine aggregate.

Aggregate 2 was chosen as a moderately reactive aggregate which was confirmed through the accelerated mortar bar test. Figure 2.2 displays the 28 day expansion results with mixtures incorporating 0%, 25%, 35% and 45% replacements of FA2 and FA5.

(a)

(b)
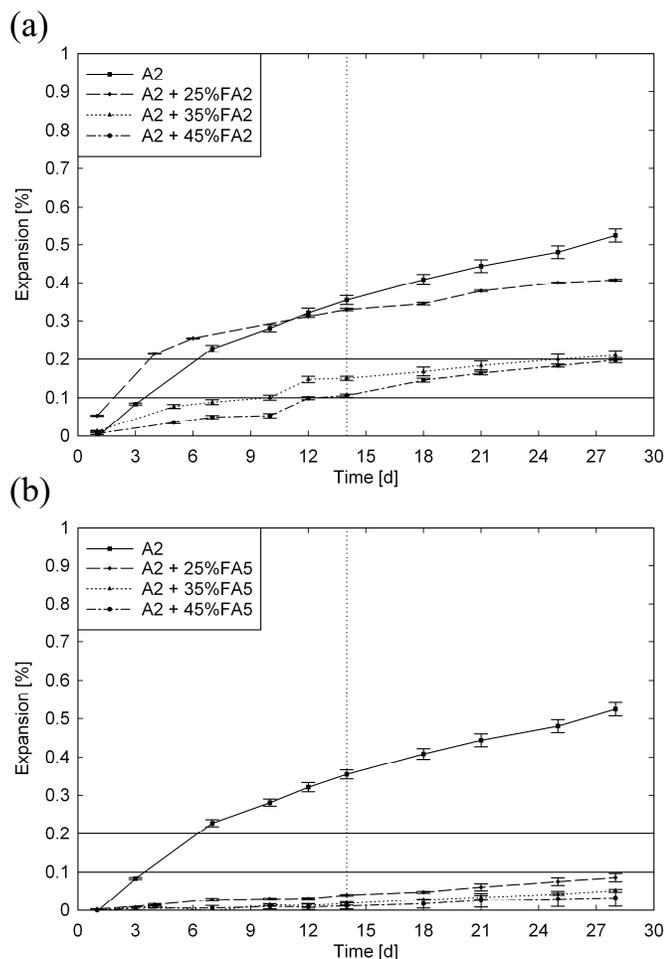
Figure 2.2 – Aggregate 2 with 0%, 25%, 35% and 45% replacement levels of a) FA2 and b) FA5

Figure 2.2a shows that FA2 was capable of reducing expansion at all replacement levels investigated although even 35% replacement was not sufficient to mitigate expansion below the 0.1% limit at 14 days. It should be noted that a replacement level of 25% of the high alkali FA2 actually resulted in an increase in early-age expansion above that of the control mix (e.g. <10 days). This could be a result of the high level of alkali from this fly ash contributing to expansion where at higher replacement levels (e.g. 35 and 45%) the dilution effect of the ash and the added pozzolanic activity actually work to reduce expansion due to ASR. As shown in Figure 2.2b, all replacement levels of FA5 are sufficient for mitigating ASR expansion below the 14-day limit of 0.1% and even at 28 days this ash was effective in reducing expansion below 0.1% at all levels investigated.

Overall, the accelerated mortar bar tests confirmed that increasing the fly ash replacement level effectively decreased expansion due to alkali silica reaction. All fly ashes mixed with either a highly reactive or a moderately reactive aggregate effectively reduced expansion with a direct correlation between level of replacement and expansion mitigation. In general, the fly ashes with high alkali contents did not perform as well as fly ashes with moderate or low alkali concentrations. This is anticipated to be due to the increase of alkalies drawn into pore solution, thus promoting greater reactivity. Assessment of the available alkali concentration from the fly ash to the pore solution is necessary to determine whether this is the true case, but the correlation from the collected AMBT results support the explanation.

2.5.2   Fly ash chemistry and 14-day expansions

Correlations were drawn between the AMBT expansion results and the fly ash chemistry. Of particular interest were the relationships between the 14-day expansions (current limits set forth in ASTM C 1567) and the total alkali and CaO contents of the different fly ashes in the study.

Figure 2.3 displays the total alkali content of the various fly ashes (25, 35 and 45% replacement levels) plotted against 14-day expansion results for mortar mixtures containing Aggregate 1, while Figure 2.4 correlates the CaO content of the fly ash with the 14-day expansion results. The black diamond denotes the control mix, and thus represents the alkali content of the raw cement.
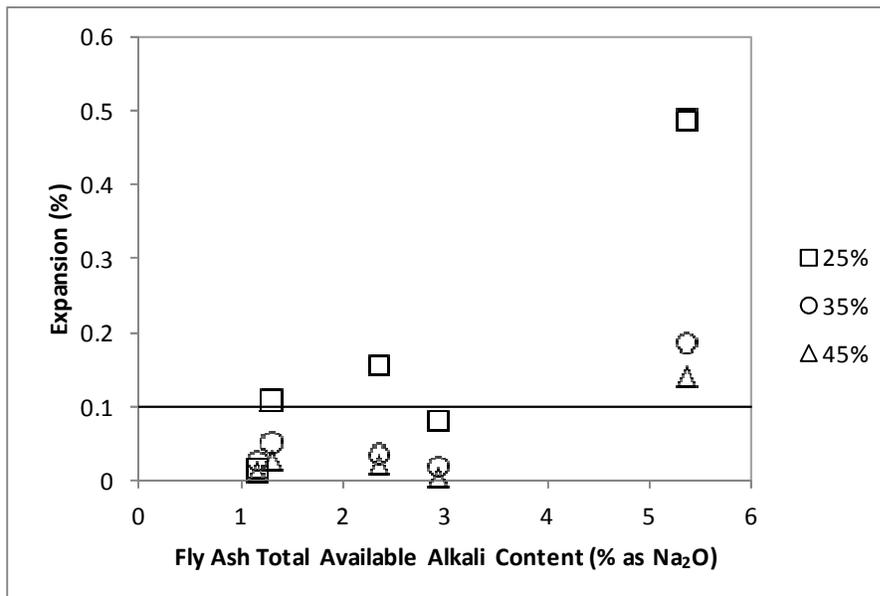
Figure 2.3 - 14-day expansions versus total available alkali content of the raw fly ash
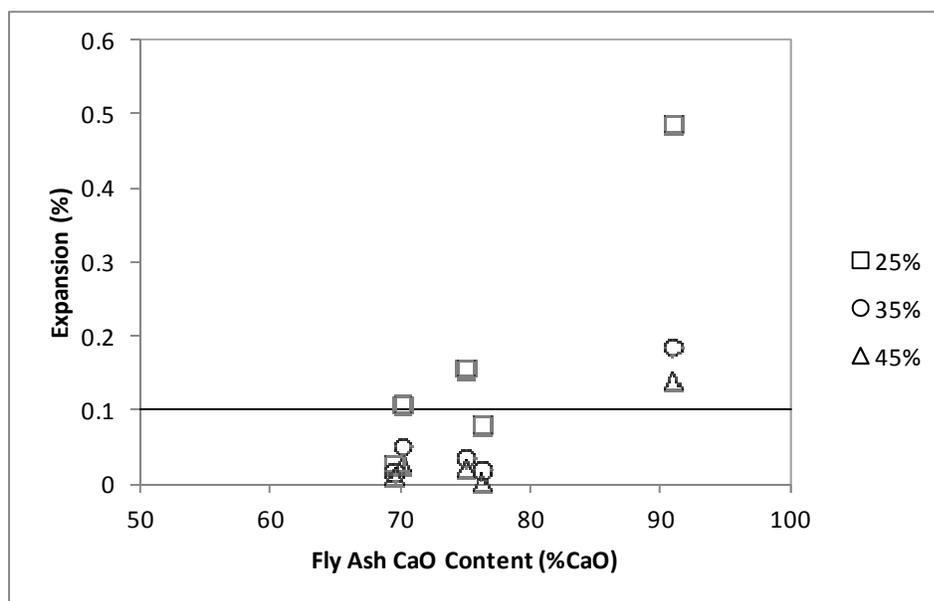
Figure 2.4 - 14-day expansion results related to CaO content of the raw fly ash

As depicted by Figure 2.3, as the replacement level of fly ash increased the resulting ASR expansion generally decreased. However, in the case of the fly ash with high alkali content even the highest replacement level (45%) was not sufficient to control the reaction below 0.1% expansion. In fact, the higher alkali content at a 25% replacement

level resulted in a rather high expansion of 0.5% which would clearly not provide protection against deleterious ASR. Figure 2.4 shows a similar trend to Figure 2.3 as the efficiency of the ash becomes less as the CaO content increases. In most ashes with a CaO content below 15% a replacement level of 35% and 45% were sufficent to control the reaction to less than 0.1% expansion at 14 days. However in the case of the fly ash with a high CaO content even a 45% replacement level was not able to control deleterious expansion.

2.5.3   Incremental Expansions

From the data collected in the accelerated mortar bar test, incremental expansion rates were calculated which describe the day-to-day expansion of the mortar bars. Results of mixtures made with Aggregate 1 and Aggregate 2 combined with FA2 are presented below in Figure 2.5.
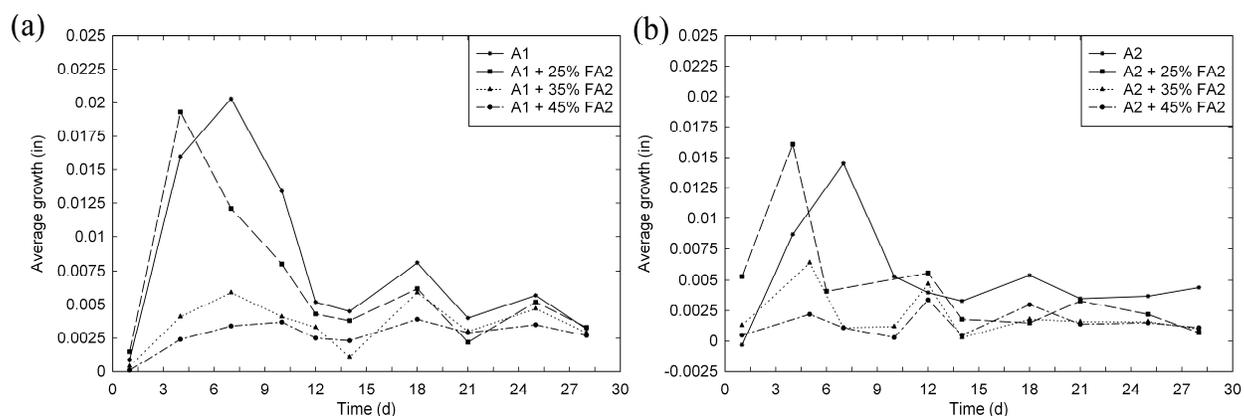
Figure 2.5 – Incremental growth rates of a) A1 with FA2 and b) A2 with FA2

These trends clearly show that the majority of expansion occurred in the first 14 days of the test, and gradually reduced after that time period. Mortar bars with no fly ash replacement (control mixes) resulted in an average of 77% of 28-day expansion occurring in the first 14-days of the 28-day test. The results displayed in Figure 2.5, collected from the most reactive of the mixes, support the current duration of the AMBT at 14 days. For the less reactive mixes the incremental growth tended to follow a linearly increasing

curve, however, this is not of concern as the expansion remained below the 0.1% expansion limit throughout the course of testing.

2.5.4 Fly Ash Chemical Index Characterization

In the development of the chemical index, Malvar and co-workers divided the fly ash chemical constituents into two groups: those that increase expansion and those that decrease expansion. Constituents that increased expansion included CaO, Na_2O, K_2O, MgO, and SO_3, while those that decreased it consisted of SiO_2, Al_2O_3, and Fe_2O_3.[13] As mentioned previously, CaO has been recognized as having one of the most significant effects on ASR expansion and has often been used in relation to silica in the ratio CaO/SiO_2.[1] Thus, a calcium oxide equivalent was represented as a combination of the CaO molar equivalents of the deleterious constituents including, SO_3, and MgO.[13] With respect to constituents which reduced expansion (SiO_2, Al_2O_3, and Fe_2O_3), SiO_2 was considered the most beneficial in preventing expansion caused by alkali silica reaction. Therefore, Al_2O_3 and Fe_2O_3 were replaced by their SiO_2 molar equivalents and were then applied to the CaO_{eq}/SiO_{2eq} relationship. Malvar et al. compared the ratio with normalized expansion values using the 14-day AMBT method. To account for reactivity of the constituents, they introduced two weighting factors (α and β) in the CaO and SiO_2 equivalencies, which replaced the previous CaO_{eq}/SiO_{2eq} ratio with a chemical index for the blend C_b. The same chemical index can be defined for a blend with no fly ash replacement (0% ash), which is defined as C_c in Equation 2.3 or for a blend with purely fly ash and no cement (100% ash) as denoted by C_{fa} in Equation 2.4.[13]

$$C_c = \frac{CaO_{eq\alpha c}}{SiO_{2eq\beta c}} = \frac{CaO + 6.0\left(0.905Na_2O + 0.595K_2O + 1.391MgO + 0.700SO_3\right)}{SiO_2 + 1.0\left(0.589Al_2O_3 + 0.376Fe_2O_3\right)} \qquad \textbf{Eq. 2.3}$$

$$C_{fa} = \frac{CaO_{eq\alpha fa}}{SiO_{2eq\beta fa}} = \frac{CaO + 6.0\left(0.905Na_2O + 0.595K_2O + 1.391MgO + 0.700SO_3\right)}{SiO_2 + 1.0\left(0.589Al_2O_3 + 0.376Fe_2O_3\right)} \qquad \textbf{Eq. 2.4}$$

Using these correlations, Malvar and Lenke determined the amount of fly ash that should be used to produce a mixture with a low risk for ASR based on the chemistry of the fly ash, the reactivity of the aggregate (determined by ASTM C 1260) and the constituents of the particular cement. This was achieved by determining the effect of the C_b/C_c ratio on 14-day AMBT expansion, where the maximum ASTM C 1260 14-day expansion sought was 0.08%. The definition of this ratio incorporated an inverse hyperbolic tangent function as shown in Equation 2.5. Using this equation, the necessary fraction of fly ash to limit expansion to 0.08% with either 50% or 90% reliability was calculated using Equation 2.6. Where, W was the weight fraction of the ash constituent and E_{14c} is the expansion of a mixture with cement only. Equation 2.6 gives the minimum required fly ash replacement as a function of the chemistry of the fly ash ($CaO_{eq\alpha fa}$ and $SiO_{2eq\beta fa}$), the cement chemistry ($CaO_{eq\alpha c}$ and $SiO_{2eq\beta c}$), and the 14-day AMBT expansion with cement only (E_{14c}).

$$\frac{C_b}{C_c} = g\left(\frac{0.08}{E_{14c}}\right) = a_4 \tanh^{-1}\left(\frac{2\left(0.08/E_{14c}\right) - \left(a_1 + a_2\right)}{a_2 - a_1}\right) + a_3 \qquad \textbf{Eq. 2.5}$$

$$W = \frac{1 - g\left(0.08/E_{14c}\right)}{\left(1 - \dfrac{CaO_{eq\alpha fa}}{CaO_{eq\alpha c}}\right) - \left(1 - \dfrac{SiO_{2eq\beta fa}}{SiO_{2eq\beta c}}\right)g\left(0.08/E_{14c}\right)} \qquad \textbf{Eq. 2.6}$$

The procedure outlined by Malvar et al. was applied to the materials and results of ASTM C 1260 testing. The index was used to calculate the minimum required fly ash replacement levels necessary to limit AMBT expansion to 0.08% based on the chemical composition of the cement and fly ash and the values were compared against the performed AMBT results. This was done in an effort to determine the efficacy of this method for fly ashes with moderate to high calcium oxide contents and moderate to high alkali contents. Fly ash and cement chemical constituents, analyzed by a professional

analytical laboratory, were utilized in Equations 2.3-2.6 to establish resulting suggested replacement levels. The coefficients outlined in Table 2.4 were applied based on the reliability curves calculated by Malvar et al.[13]

Table 2.4. Reliability Coefficients Provided by Malvar et al.[13]

Calculation Coefficients	90% Reliability	50% Reliability
$E_{14\sigma\text{-}A1}$	0.6290	0.6290
$E_{14\sigma\text{-}A2}$	0.2797	0.2797
α	6	6
β	1	1
a_1	0	0
a_2	1.0244	1.053
a_3	0.6696	0.7386
a_4	0.1778	0.1778

$E_{14\sigma}$ = 14-day AMBT expansion with cement only

The coefficients are shown for 50% and 90% reliability curves. The coefficients for the 90% reliability curves have a significant safety factor that increases as the C_{fa} value increases (e.g. it is much higher for Class C ashes as these are well established to be less effective in mitigating ASR).[3] The 50% reliability curve does not have a "built-in" safety factor; it is the best prediction possible given the dataset used to calibrate the model. As a result both the 50% and 90% predictions are included to assess (1) the best prediction (using the 50% reliability curves), and (2) the safety included in the 90% prediction for this study. Results are presented in

Table 2.5 for fly ash efficiency tested with the A1 and A2 fine aggregates.

Table 2.5. Material Chemical Index and Minimum Predicted Fly Ash Replacement, W for 50 and 90% Reliability

Material	Ash Type (ASTM)	Chemical index C_{fa} index C_c	W with A1	W with A2	W with A1	W with A2
			50% Reliability		90% Reliability	
FA1	F	1.220	0.417	0.294	0.532	0.382
FA2	C	2.480	1.621	1.01	2.358	1.431
FA3	F	1.110	0.373	0.263	0.476	0.342
FA4	F	0.610	0.261	0.187	0.327	0.240
FA5	F	0.270	0.222	0.161	0.284	0.219
Cement	Type I	3.626				

This methodology predicted that a 38.2% replacement of FA1was necessary to reduce expansion levels below 0.08% when using A2 fine aggregate and that a 53.2% replacement was needed when using A1 fine aggregate following the 90% reliability curves. Similarly, the method predicted that a 34.2% and 47.6% replacement of FA3 with A2 and A1 aggregates, respectively, was needed to reduce expansions below 0.08%. For the FA4 fly ash a replacement level of 24% and 32.7% for A2 and A1 fine aggregates, respectively, were necessary to reduce expansion below 0.08%. Lower values were predicted for 50% reliability (e.g. actual prediction without safety factors). In particular it was predicted that approximately 29.4% FA1, 26.3% FA3 and 18.7% FA4 fly ashes were needed to reduce expansions below the 0.08% limit for the A2 fine aggregate. For the highly reactive A1 aggregate lower values were also predicted for FA1, FA3 and FA4 ashes. While the values for the 90% reliability curve predictions are reasonable they do represent conservative values where experimental results showed lower levels of FA3 and FA4 were necessary to control the reaction (in the case of the 90% reliability curves). Using the 50% reliability curves data were more closely aligned with experimental results. However, for FA2, this approach resulted in a suggested replacement level of 143.1% when used with A2 aggregate and 235.8% with the A1 aggregate for the 90% reliability curves and 101% and 162% for the 50% reliability curves which is not in line with experimental results. This is a result of the chemical constituents of the FA2 fly ash, particularly the high levels of total alkalies and calcium oxide (CaO). Figure 2.6 displays the effect the inverse hyperbolic tangent function has on the suggested minimum fly ash replacement level (W) as a function of the fly ash CaO content for 50% reliability predictions.

Figure 2.6. Suggested Minimum Fly Ash Replacement Level, *W*, as a Function of the Fly Ash CaO Content using FA2 Fly Ash Chemical Constituents and 50% Reliability.

This graph was constructed by holding all FA2 fly ash (CaO 27.06%) chemical constituents constant except for CaO, which is analyzed from 2 to 100%, and then the value of *W* was determined using Equations 2.3-2.6. The graph shows that as the calcium oxide content increases, so does the minimum replacement level, until a point at which a vertical asymptote is reached and *W* goes towards infinity. The region of interest, however, is between 0% and 20% CaO where the suggested fly ash replacement level exceeds 50% even for a low CaO ash. At approximately 10% CaO content about 60% of that ash would be needed to control the reaction. Clearly this not representative of the actual level of FA2 needed to control the reaction, however, it does show the impact that an ash with high levels of ASR-promoting constituents has on its ability to control ASR based on this model.

Figure 2.7 shows the same relationship for FA3 (CaO 11.16%) again holding all chemical constituents of FA3 constant while the amount of CaO varies from 2 to 100%.

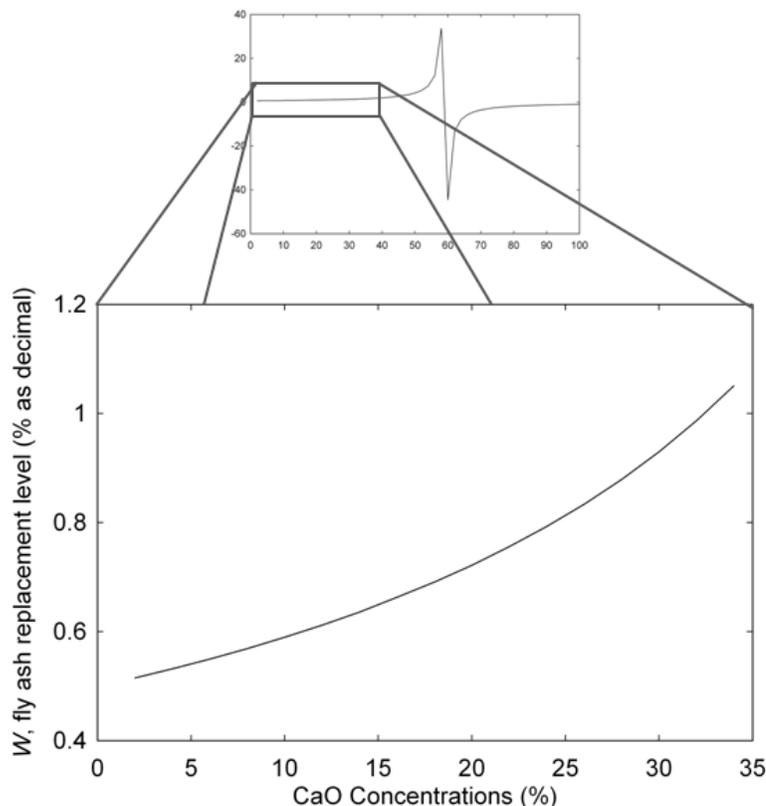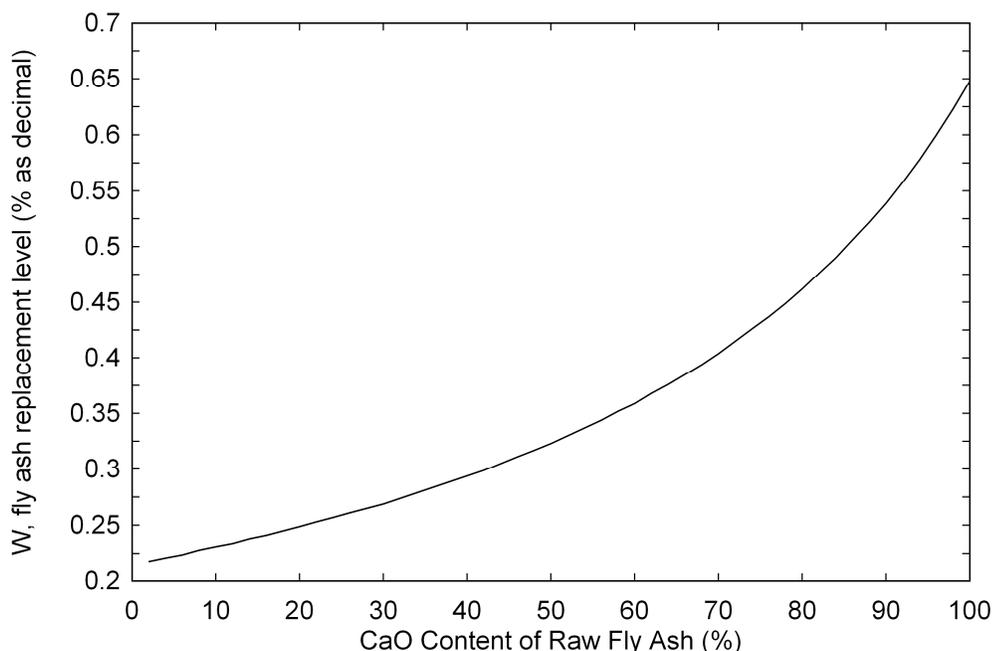**Figure 2.7. Suggested Minimum Fly Ash Replacement Level, *W*, as a Function of the Fly Ash CaO Content using FA3 Chemical Constituents using 50% Reliability Curves**

The discrepancy between the two graphs is significant. When the CaO content of FA3 approaches 30% the suggested replacement level, *W*, is only around 25% whereas with the FA2 fly ash *W* approaches 60% when the CaO content is around 10%. This trend, a result of the prediction model, points to the profound impact that higher alkali and CaO concentrations in the ash have on the ability of the ash to control alkali silica reaction which is evidenced, although to a much lower extent, in laboratory testing. Modifications to this fly ash chemical index approach may be necessary when ashes similar to FA2 (higher CaO and moderate alkali contents) are analyzed. In fact an entirely different approach may be necessary to adequately characterize the amount of fly ash (similar in chemical composition to FA2) that would be needed to control deleterious ASR. On the other hand, this could be as simple as optimizing the weight (currently 6.0) in front of the alkali and CaO contents in Equations 2.3 and 2.4. Eventually this may need an alternate calibration approach using a new test method more sensitive to the ash alkali content.

Comparisons were also made between the CaO and Na_2O constituents of the fly ashes used in the study and the suggested fly ash replacement levels as shown in Figure 2.8, below.
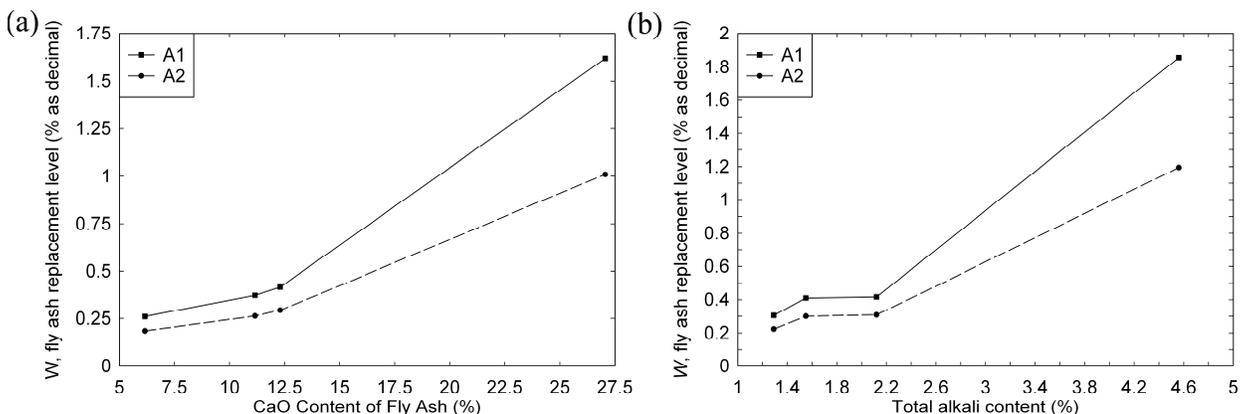
Figure 2.8. Plot of the Suggested Minimum Required Fly Ash Replacement as a Function of a) the CaO Content of the Fly Ash and b) the Total Alkali Content of the Fly Ash using 50% Reliability Curves.

Consistently, increasing contents of both CaO and Na_2O result in a higher suggested replacement level of fly ash in order to keep 14-day expansion levels below 0.08%. It can also be noted that, in both graphs, the A1 aggregate requires greater fly ash replacement than the A2 aggregate, which is a result of the higher alkali-silica reactivity and thus higher AMBT expansion results at 14 days of the A1 aggregate.

Figure 2.9 displays the expansion results from A1 aggregate with 0%, 25%, 35% and 45% replacement levels of FA3 and A2 aggregate with the same replacement levels of FA3. The horizontal dashed line at 0.08% represents the expansion limit used by Malvar and coworkers in the derivation of the chemical matrix predictive equations.
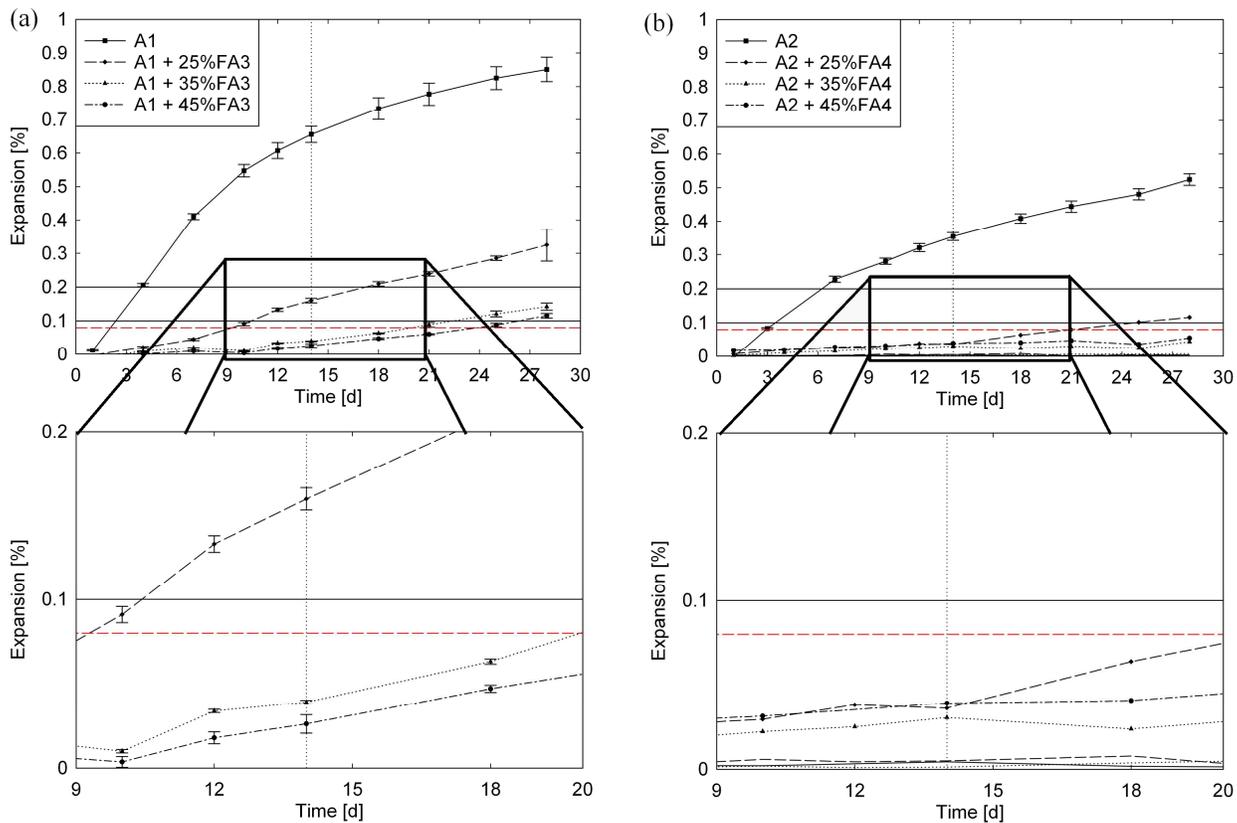
Figure 2.9. ASTM C 1567 results with a) A1 aggregate and FA3 and b) A2 Aggregate and FA4

ASTM C 1567 results performed in the lab were compared with the fly ash chemical index results. Predictions of the fly ash replacement levels needed to hold expansion to 0.08% or lower were done using the *Statgraphics* computer program. A plot was made of the 14-day expansion values and the corresponding replacement levels tested in the lab and an exponential curve was created with prediction limits set at 50% confidence. From this curve the replacement level to maintain an expansion of 0.08% was then extrapolated. Table 2.6 provides the predicted replacement levels of the experimental data and the suggested fly ash replacement levels calculated from the Malvar et al. chemical index. Table 2.7 supplies the 50% confidence intervals for each curve.

Table 2.6. Fly ash replacement levels predicted from experimental results and Malvar et al. procedure

Material	Predicted replacement levels to maintain expansion <0.08% based on fly ash chemical index from Malvar et. al				Predicted replacement levels to maintain expansion <0.08% based on experimental data	
	90% Reliability		**50% Reliability**			
	A1	**A2**	**A1**	**A2**	**A1**	**A2**
FA1	53.2	38.2	41.7	29.4	33.72	21.25
FA2	235.8	143.1	162.7	101	57.76	33.93
FA3	47.6	34.2	37.3	26.3	39.63	25.92
FA4	32.7	24	26.1	18.7	36.72	16.68
FA5	28.4	21.9	22.2	16.1	24.32	17.35

Material	Predicted replacement levels to maintain expansion <0.08% based on fly ash chemical index from Malvar et. al			
	90% Reliability		**50% Reliability**	
	A1	**A2**	**A1**	**A2**
FA1	53.2	38.2	41.7	29.4
FA2	235.8	143.1	162.7	101
FA3	47.6	34.2	37.3	26.3
FA4	32.7	24	26.1	18.7
FA5	28.4	21.9	22.2	16.1

Table 2.7. Prediction limits of experimental material

Fly Ashes		Predicted replacement levels to maintain expansion <0.08% based on experimental data	
		A1	**A2**
	Mean	33.72	21.25
FA1	50% Low	28.81	17.72
	50% High	39.46	25.48
	Mean	57.76	33.93
FA2	50% Low	46.68	27.39
	50% High	71.47	42.03
	Mean	39.63	25.92
FA3	50% Low	32.31	18.75
	50% High	48.60	35.83
	Mean	36.72	16.68
FA4	50% Low	35.00	11.30
	50% High	38.52	24.60
	Mean	24.32	17.35
FA5	50% Low	17.60	15.51
	50% High	33.60	19.39

Predictions made using the chemical index calculations based on 90% reliability were overly conservative compared to experimental results. However, the predictions using 50% reliability closely aligned with those of the experimental, particularly for the mixes with FA3 and FA5 ashes and to a lesser extent with FA1 ash. It is clear that for the FA2 fly ash the chemical index equations proved unsuccessful as neither reliability limit produced reasonable replacement values since all were above 100%, while the experimental prediction values were about 58% and 34% for A1 and A2 respectively. Therefore, modifications should be made to this methodology when assessing ashes with increasing amounts of "ASR promoting" compounds such as CaO, Na_2O and K_2O. This may simply involve recalibration of the coefficients using an expanded database which includes such ashes.

The fly ash chemical characterization index shows promise for low alkali and low CaO fly ashes, however, for borderline ashes with moderate to high alkali and/or high calcium concentrations the index does not provide reliable results. The index has strong correlation with ASTM C 618 as well as the related Canadian Standards.[13] However, ASTM C 618 does not include any requirements regarding the limits of available alkalies from fly ash. Values reported in work by Malvar and co-workers were obtained from their referenced sources.[13, 17] Thus, it is necessary to establish a rapid test method to confidently determine the alkali contribution from the fly ash, which could then be implemented into this index. Determining the true alkali contribution from fly ash and incorporating that value into the chemical index would provide reliable information for the calculation of the minimum fly ash replacement level to successfully mitigate expansion due to alkali silica reaction.

2.6   Conclusions

The results presented show that the accelerated mortar bar test is a useful method for determining the effectiveness of fly ash to mitigate expansion due to alkali silica reaction. In addition, the chemical index proposed by Malvar et al. shows promise in calculating a suggested fly ash replacement value determined by the chemical makeup of the materials

as well as the 14-day AMBT results of the aggregate. Comparisons between ASTM C 1567 results with and without fly ash as well as predictions calculated with the method developed by Malvar et al. produced the following conclusions:

- All fly ashes used in this study decreased ASR related expansion
- Increasing the level of fly ash effectively reduced expansion due to alkali silica reaction
- Efficacy of fly ash to mitigate expansion decreased as both the raw fly ash alkali and CaO contents increased
- Incremental growth curves proved that a majority of expansion occurred in the first 14-days of the accelerated mortar bar test
- For low alkali and low calcium fly ashes the chemical index introduced by Malvar et al. produced similar predictions for the fly ash replacement level necessary to maintain expansion levels below 0.08% with 50% reliability compared to the experimental results
- For fly ashes with moderate to high alkali and calcium concentrations the chemical index is not sufficient for predicting the replacement level necessary to mitigate ASR expansion below 0.08%

The accelerated mortar bar test effectively demonstrates that fly ash is useful in mitigating alkali silica reaction in the samples tested. However, the overwhelming nature of the 80 °C 1N NaOH soak solution does not allow for a true assessment of the alkali contribution of fly ash due to the high alkalinity. Malvar and coworkers have developed a promising technique for predicting fly ash replacement levels, however, modifications are needed to accurately include all fly ashes, particularly borderline ashes. Further assessment of the alkali contribution from fly ash is necessary to determine the role these anions play in alkali silica reaction. Such research is currently taking place at the authors' laboratories.

2.7 References

1. Folliard, K.J., et al., *Interim Recommendations for the Use of Lithium to Mitigate or Prevent Alkali-Silica Reaction (ASR)*. July 2006, Federal Highway Administration.
2. Kosmatka, S.H., *Design and Control of Concrete Mixtures*. 14 ed. 2008, Skokie, Illinois: Portland Cement Association.
3. Shehata, M.H., M.D.A. Thomas, and R.F. Bleszynski, *The Effects of Fly Ash Composition on the Chemistry of Pore Solution in Hydrated Cement Pastes.* Cement and Concrete Research, 1999. **29**: p. 1915-1920.
4. Glasser, F.P., ed. *Chemistry of the Alkali-Aggregate Reaction*. The Alkali-Silica Reaction in Concrete, ed. R.N. Swamy. 1992: Blackie, London, United Kingdom. 96-121.
5. Diamond, S., *Effects of two Danish fly ashes on alkali contents of pore solutions of cement fly ash pastes.* Cement and Concrete Research, 1981. **11**(3): p. 383-94.
6. Taylor, H.F.W., *A method for predicting alkali ion concentrations in cement pore solutions.* Advances in Cement Research 1987. **1**: p. 5-16.
7. Chen, W. and H.J.H. Brouwers, *Alkali binding in hydrated Portland cement paste.* Cement and Concrete Research, 2009. **40**: p. 716-722.
8. Thomas, M. and M. Shehata, *Use of Blended Cements to Control Expansion of Concrete due to Alkali-Silica Reaction*, in *Eighth CANMET/ACI International Conference on Flyash, Silica Fume, Slag And Natural Pozzolans in Concrete*, P. Gupta, Editor. 2004: Las Vegas, U.S.A. p. 591-607.
9. Shehata, M.H. and M.D.A. Thomas, *Alkali release characteristics of blended cements.* Cement and Concrete Research, 2006. **36**: p. 1166-1175.
10. Thomas, M.D.A. and F.A. Innis, *Use of the Accelerated Mortar Bar Test for Evaluating the Efficacy of Mineral Admixtures for Controlling Expansion due to Alkali-Silica Reaction.* Cement, Concrete, and Aggregates, 1999. **21**: p. 157-164.
11. *Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)*, in *ASTM C1260-07*, A. International, Editor. 2009, ASTM Int'l West Conshohocken, PA.
12. Thomas, M.D.A., et al., *Performance Limits for Evaluating Supplementary Cementing Materials using the Accelerated Mortar Bar Test. PCA R&D*, 2005(2892).
13. Malvar, L.J. and L.R. Lenke, *Efficiency of Fly Ash in Mitigating Alkali-Silica Reaction Based on Chemical Composition.* ACI Materials Journal, 2006. **103**(5): p. 319-326.
14. ACI, C., *State-of-the-Art Report on Alkali-Aggregate Reactivity (221.1R-98).* 1998, American Concrete Institute: Farmington Hills, Mich. p. 31.
15. Malvar, L.J., et al., *Alkali-Silica Reation Mitigation: State of the Art and Recommendations.* ACI Materials Journal, 2002. **99**(No. 5): p. 480-489.
16. *Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar*

Method), in *ASTM C 1567*. 2008, ASTM International: West Conshohocken, PA. p. 6.

17.   *ASTM C618 Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, in *ASTM C618-09*, A. International, Editor. 2009, ASTM International: West Conshohocken, PA.

Fly Ash and the Mitigation of Alkali-Silica Reaction: Alkali Availability

Kelsea A. Schwing, Jason H. Ideker

3 Second Manuscript

Fly Ash and the Mitigation of Alkali-Silica Reaction: Alkali Availability

Kelsea Schwing[1], Jason H. Ideker[2]

Abstract: This paper discusses the results of an experimental program designed to characterize the binding of alkalies (Na^+ and K^+) within the hydration products of cement and fly ash paste samples. The study was done in two parts: first, chemical analysis of pore solution from paste was analyzed from samples made with select replacement levels of various fly ashes subjected to various curing conditions. Part two related the quantitative pore solution analyses with results from a series of ASTM C 1567 expansion tests to determine the effectiveness of the fly ashes to mitigate alkali-silica reaction. Results showed that over time low alkali ashes were better able to bind alkalies, however increasing the replacement level of high alkali ashes resulted in a decrease of free alkalies in the pore solution. The ability of an ash to control ASR expansion appears to also be strongly influenced by the alumina content of the raw fly ash. Further research into the role that alumina plays in limiting deleterious ASR as well as the mineralogical makeup of fly ash will assist in the development of a rapid test method to accurately determine alkali contribution from fly ash to concrete pore solution.

Keywords: Alkali-Silica Reaction, Fly Ash, Alkali Availability.

---

[1] Graduate Research Assistant, School of Civil and Construction Engineering, Oregon State University, USA; E-mail: kelsea2122@gmail.com

[2] Assistant Professor, School of Civil and Construction Engineering, Oregon State University, USA; E-mail: jason.ideker@oregonstate.edu

3.1   Introduction

Alkali-silica reaction (ASR) is an internal chemical reaction in concrete which can lead to severe cracking of both structural and non-structural elements. It is the high pH of the concrete pore solution (typically between 13.2 and 13.8) which drives the reaction. The high pH is caused by the presence of alkalies (Na_2O and K_2O) primarily provided by the portland cement, and as the alkalies disassociate in pore solution, the positively-charged Na^+ and K^+ must be balanced by the same magnitude of negative charges, principally hydroxyl (OH^-) ions. Three conditions are necessary for ASR gel to be formed: (1) available alkalies in the pore solution; (2) reactive silica present in the aggregates; and (3) sufficient moisture available to drive the reaction. If all three of these conditions are met, the OH^- ions attack the reactive silica, after which the Na^+ and K^+ ions and lesser amounts of calcium combine with the reaction products to form a gel-like material. ASR gel has a high affinity to absorb water, and if water is available (from pore solution or external sources), the gel will expand, putting the concrete in tension.[1] If the tensile forces exceed the tensile strength of the concrete, cracking can occur, thus allowing for more accessibility of water, exacerbating ASR and other deterioration mechanisms such as corrosion of embedded steel reinforcement or freeze-thaw attack. Eliminating any of the three conditions necessary for ASR (sufficient alkalies, reactive silica, and available moisture) will eliminate expansion due to alkali-silica reaction. However, it may be challenging, and in fact impossible, to eliminate all or even any of these conditions and doing so may induce other detrimental factors for the concrete. Therefore, much attention has been focused in the past 70 years on other mitigation strategies to eliminate or at the very least, reduce the risk of deleterious ASR.[2-8]

One of the most common mitigation strategies involves the use of supplementary cementing materials (SCMs), particularly fly ash. Research has shown that the efficacy of SCMs to mitigate ASR expansion is strongly linked to their ability to lower the level of alkalinity of the concrete pore solution.[9-11] Hydration products, primarily C-S-H, of systems containing portland cement and certain SCMs have a decreased Ca/Si atomic ratio than systems without SCM, and this improves the ability of C-S-H to bind alkalies

and thus decrease their availability in the pore solution.[7, 12, 13] However, SCMs also contain alkalies and, particularly for fly ash, the amount may be more than that present in the portland cement. For example, as documented by Shehata and Thomas, analysis of more than 100 North American fly ashes showed alkali contents ranging from 1.0% to almost 10%, with an average of 2.44% sodium oxide equivalent (Na_2O_e).[7] Some of this alkali content may remain bound in crystalline products within the hydrated cement paste and thus not be available to react with the aggregates, and therefore it is important to be able to determine how much alkali will be truly available to the concrete pore solution from a given SCM. This is the goal of tests such as the available alkali test in ASTM C 311. In short, this test calls for mixing 5 g of SCM (such as fly ash) with 2 g of hydrated lime and 10 mL of water and then storing the mixture in a sealed container for 28 days at a temperature of 38 ^{o}C. After this time, the samples are ground with water, making a slurry that is then leached into 200 mL of water for 1 hr. The sample is then filtered, the residue washed 8 to 10 times with hot water and then the sodium and potassium concentrations are determined. The drawback of this test is that the leaching solution of distilled water is of essentially neutral pH, drawing more alkalies into the solution than would be available in the high pH of the pore solution of concrete. Also, if this test is performed for an extended period of time (i.e. many months) virtually all of the alkalies are released.[14] Thus, the available alkali test of ASTM C 311 tends to over-estimate the available alkali contribution from fly ashes.

Another standard which once addressed the available alkali content from fly ash is ASTM C 618, the Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. In the 2000 revision, this standard outlined an optional available alkali content requirement of 1.5% as equivalent Na_2O, applicable only when specifically required by the purchaser. However, this requirement was deleted in the following edition (ASTM C 618-01) and in successive standards the only requirement related to alkali-silica reaction were 14-day expansion values (in ASTM C 1567), also optional.[15] This lack of consistency in the regulations proves that no agreed upon test methods or strategies exist for determining the available alkali contribution from fly ash.

Thus, a rapid test method to accurately determine the available alkali content from fly ash to the pore solution of concrete is in need and is the basis of this study.

3.2   Research Significance

The purpose of this study was to determine the relation between pore solution chemistry of cement-fly ash pastes samples and accelerated mortar bar expansion results.   In addition, this studied aimed to better understand the ability of hydration products to bind alkalies in systems made with fly ash as a supplementary cementing material. Successful determination of the alkali binding characteristics of a cement-fly ash mixture will aid in the development of a rapid test method to accurately detect the available alkali contribution from fly ashes to the pore solution of concrete.

3.3   Materials and Experimental Procedure

3.3.1   Pore Solution Evaluation from Paste Samples

The materials for this project were chosen carefully to ensure a wide range of chemical constituents in the fly ash and cement samples. Two ASTM C 150 Type I cements were used, one with a high alkali content and one with a low alkali content. The fly ashes used included those which have already shown promise for mitigating ASR, ashes which are considered "border line ashes", as well as those that are considered to be ineffective in controlling ASR at standard dosage rates (e.g. 15-35%). The chosen fly ashes were carefully considered based on their alkali and calcium contents. Table 3.1 provides the entire oxide analysis for the chemical constituents of the fly ashes and portland cements used as determined by an independent testing laboratory.

Table 3.1. Chemical composition of materials (mass %)

Constituent (Wt%, dry basis)	FA1	FA2	FA3	FA4	FA5	Cement 1	Cement 2
SiO_2	47.66	33.16	54.06	63.95	59.36	20.08	21.79
Al_2O_3	21.58	17.04	16.36	16.54	25.14	5.61	3.89
Fe_2O_3	4.21	4.91	6.01	4.43	5.56	2.51	2.95
$SiO_2+Al_2O_3+Fe_2O_3$	73.45	55.11	76.42	84.92	90.06		
CaO	12.3	27.06	11.16	6.16	5.63	63.79	64.1
MgO	2.70	5.06	4.14	2.38	0.94	1.22	1.40
Na_2O	6.02	5.09	3.30	2.31	0.40	0.13	0.30
K_2O	0.89	0.78	1.86	1.47	0.97	1.00	0.41
TiO_2	0.97	1.11	0.98	0.90	1.09	0.24	0.27
MnO_2	0.02	0.05	0.10	0.05	0.08	0.05	0.09
P_2O_5	0.47	0.51	0.29	0.30	0.03	0.29	0.15
SrO	0.42	0.61	0.32	0.21	0.11	0.09	0.05
BaO	0.80	1.17	0.55	0.46	0.16	0.02	0.12
SO_3	1.20	2.87	0.64	0.54	0.37	3.39	2.55
LOI	0.76	0.58	0.24	0.31	0.16	1.59	1.94
Moisture, as received	0.09	0.15	0.06	0.04	0.04		
Na_2O^a	1.93	4.20	1.18	0.95	0.15		
K_2O^a	0.29	0.54	0.56	0.52	0.31		
$Na_2O_e^b$	6.61	5.60	4.52	3.28	1.04	0.79	0.57
C_3S						56.20	57.78
C_3A						10.61	5.31
C_2S						15.17	18.87
C_4AF						7.64	8.97

[a] Available alkali, as per ASTM C311

[b] Total alkali ($Na_2O+0.658K_2O$)

Paste samples (water and cementitious materials only) for pore solution analysis were cast with cement and 0%, 15%, 25%, and 35% fly ash replacement levels (by mass of total cementitious materials. All pastes and mortars were mixed using 18 MΩ deionized water in a 3-speed mixer following the mixing instructions set forth by ASTM C 305.[16] Once mixed, these samples were rotated normal to their axis for 24 hours to prevent bleeding and ensure thorough mixing prior to setting. The specimens were then stored at 23 ^{O}C, 38 ^{O}C, and 60 ^{O}C for distinct time intervals (1, 28 and 90 days) to allow progression of the hydration process and to accelerate the release of alkalies from the cementitious constituents into the pore solution. Curing at 23°C provided benchmarking data while curing at higher temperatures provided accelerated curing conditions. Upon reaching the established curing time, each paste sample was removed from the given curing temperature and the pore solution was extracted. This was performed by crushing the paste sample into fine fragments (5-20 mm in diameter), introducing these into a

hardened steel pore press (as shown in Figure 3.1), and applying a maximum force of 250,000 lbs (~63,000 psi, ~434 MPa) to express the pore solution from the paste sample which was collected in a 6 ml vial in the bottom of the pore press.

Figure 3.1: Pore solution extraction device inside compression testing machine

Once extracted, the pore solution was immediately analyzed to determine the pH using a Thermo Scientific Orion Star Plus pH meter. The pore solution was also chemically analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES Varian 150 Liberty) to determine the sodium, potassium, and calcium concentrations.

3.3.2   Accelerated Mortar Bar Test in Relation to Pore Solution Alkalinity

A series of ASTM C 1567 (Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate) accelerated mortar bar tests (AMBT) were performed in an effort to make correlations between the ability of a given fly ash to mitigate ASR and the pore solution chemistry of the fly ash-cement mixture. The procedure outlined by the ASTM C 1567 standard were followed and all sodium hydroxide solutions were titrated to ensure proper normality ($\pm$ 0.01 N).[17] Although the standard calls for a duration of 14 days exposure to 1 N NaOH, it was decided to run tests for a period of 28 days to evaluate the trends beyond the two week period. Length measurements were taken at 0, 1, 4, 7, 10, 12, 14, 18, 21, 25 and 28 days for all tests. Typical fly ash replacement levels range from 15-50% by mass, thus replacements of 25%, 35% and 45% were compared against tests run with 0% fly ash

replacement.[18] The aggregate used in this study was a highly reactive natural sand from Oregon.

3.4 Results and Discussion

3.4.1 Pore Solution Evaluation from Paste Samples

The alkali concentration of the pore solution was the primary focus of this investigation as the contribution of alkalies from fly ash (and portland cement) has one of the most significant influences on the ability of a particular ash to control alkali-silica reaction. Table 3.2 documents the results of the pore solution analysis for total alkali ($Na^+ + K^+$) and calcium concentrations for paste samples made with 0% (control) and 25% replacement of fly ashes 1-4.

Table 3.2. Select results of pore solution chemical analysis for samples made with 0% and 25% fly ash, cured at 38 ^{o}C

Sample	Temp (^{o}C)	Time (d)	Low Alkali Cement			High Alkali Cement		
			Total Alkali [$Na^+ + K^+$] (mmol/L)	Calcium (mmol/L)	pH	Total Alkali [$Na^+ + K^+$] (mmol/L)	Calcium (mmol/L)	pH
Control (0%)	23	1	142.4	1.98	13.14	396.5	0.49	13.52
		28	506.6	2.27	13.47	455.7	0.45	13.54
		90	594.4	0.98	13.35	562.6	0.29	13.67
	38	1	188.9	1.52	13.22	380.1	1.77	13.50
		28	232.0	1.01	13.21	301.4	0.47	13.48
		90	590.1	1.81	13.52	453.3	0.33	13.64
	60	1	210.7	1.23	13.24	333.9	0.79	13.42
		28	201.7	0.58	12.90	472.1	0.32	13.57
		90	609.5	2.41	13.15	390.5	0.87	13.63
FA1 (25%)	23	1	145.3	1.76	13.15	265.1	0.75	13.44
		28	261.3	0.92	13.21	405.2	0.53	13.51
		90	806.2	0.67	13.45	1026.2	0.67	13.63
	38	1	188.6	1.20	13.20	308.9	0.65	13.47
		28	344.3	0.28	13.39	465.5	0.20	13.51
		90	810.0	0.66	13.42	968.3	0.44	13.51
	60	1	321.2	0.47	13.32	388.7	0.12	13.47
		28	396.0	0.41	12.97	437.9	0.11	13.42
		90	1179.5	1.17	13.18	1169.3	0.58	13.37
FA2 (25%)	23	1	196.6	0.96	13.27	400.0	0.34	13.46
		28	378.5	1.07	13.40	664.3	0.39	13.71
		90	1369.6	1.76	13.53	1311.3	0.04	13.81
	38	1	288.9	0.74	13.35	431.0	0.20	13.55
		28	439.2	0.57	13.28	682.8	0.14	13.62
		90	1412.1	0.52	13.53	1066.2	0.31	13.68
	60	1	393.0	0.64	13.41	546.2	0.21	13.54
		28	527.8	0.66	13.35	1245.8	0.06	13.61
		90	1527.5	1.06	13.36	1684.9	0.79	13.60

Table 3.3. Select results of pore solution chemical analysis for samples made with 0% and 25% fly ash, cured at 38 °C (Continued)

		1	94.0	1.92	13.08	332.6	1.38	13.46
	23	28	487.3	1.97	13.01	315.1	0.82	13.66
		90	696.8	1.44	13.18	323.8	0.31	13.50
FA3		1	116.8	1.60	13.14	377.1	1.41	13.49
(25%)	38	28	595.2	0.69	13.05	337.3	0.24	13.49
		90	731.1	0.67	13.08	341.5	0.05	13.48
		1	206.0	0.71	13.28	513.4	0.77	13.48
	60	28	665.6	1.07	12.98	397.7	0.35	13.40
		90	883.7	1.20	13.03	480.6	0.30	13.02
		1	94.8	2.02	13.11	354.9	0.45	13.56
	23	28	416.3	2.50	13.40	449.9	1.09	13.56
		90	466.2	1.33	13.13	333.5	0.17	13.57
FA4		1	114.5	1.72	13.14	461.4	0.74	13.62
(25%)	38	28	439.3	0.70	13.38	283.8	0.15	13.48
		90	441.6	0.87	13.20	272.9	0.21	13.45
		1	164.5	0.72	13.23	499.8	0.22	13.51
	60	28	549.8	1.05	13.08	376.7	0.48	13.34
		90	497.6	1.38	13.09	272.1	0.34	13.24

For most fly ashes the alkali concentration of the pore solution increased over time, particularly in mixtures with the high alkali cement (Table 3.2). The calcium concentrations, on the other hand, tended to decrease over time at lower temperatures, but increased at elevated temperatures. Trends of these data were compared with the results of different fly ash replacement levels and are presented and discussed below.

Figure 3.2 displays changes over time of the pore solution alkali concentrations from four fly ashes at replacement levels of 25% and cured at 38 °C. Figure 3.2a represents the concentrations from pastes made with low alkali cement while results of mixtures with high alkali cement are presented in Figure 3.2b. It can be determined that at early ages (1 day) more alkalies were leached into the pore solution from pastes made with high alkali cement than those with low alkali cement. The trend is consistent for three of the samples tested at 28 days, two of high alkali content fly ashes (Total Na_2O_e 6.61% and 5.60%) and one of moderate alkali content (Na_2O_e 4.52%). Both of the low alkali content fly ashes had lower pore solution alkalinity in mixtures with low alkali cement than with high alkali cement. After a curing period of 90 days only FA1, a high alkali fly ash, resulted in a pore solution alkalinity higher with high alkali cement than with low alkali cement. The low alkali fly ash (FA4) resulted in lower 90 day alkali concentrations than

the control (no fly ash) when mixed with both the high and low alkali cements. Thus it can be determined that over time, low alkali fly ashes have better capability to bind alkalies provided by the cementitious blend. The paste samples made with high alkali fly ashes have increasing pore solution alkalinities over time both when mixed with the high and low alkali cements. The moderate and low alkali fly ashes, however, did not follow this trend and the pore solution alkalinity even decreased as hydration proceeded with the high alkali cement. The pore solution alkali concentrations of the samples made with FA2 and low alkali cement drastically increased, particularly between 28 and 90 days of curing. This is estimated to be an effect of the very high calcium content of this fly ash (CaO 27.06%) in conjunction with the presence of sulfate. As reported by Gallucci et al., in early hydration (i.e. first 48 hours) sulfur (as SO_4^{2-}) is hypothesized to be absorbed in C-S-H which creates a highly negative charge on the C-S-H surface and therefore promotes the coupled uptake of calcium (Ca^{2+}).[19] Thus, the high alkali concentration of the pore solution in the mixture with low alkali cement and FA2 is attributed to the hydration products which preferentially bound calcium instead of alkalies and hydroxides, leaving them available in the pore solution.
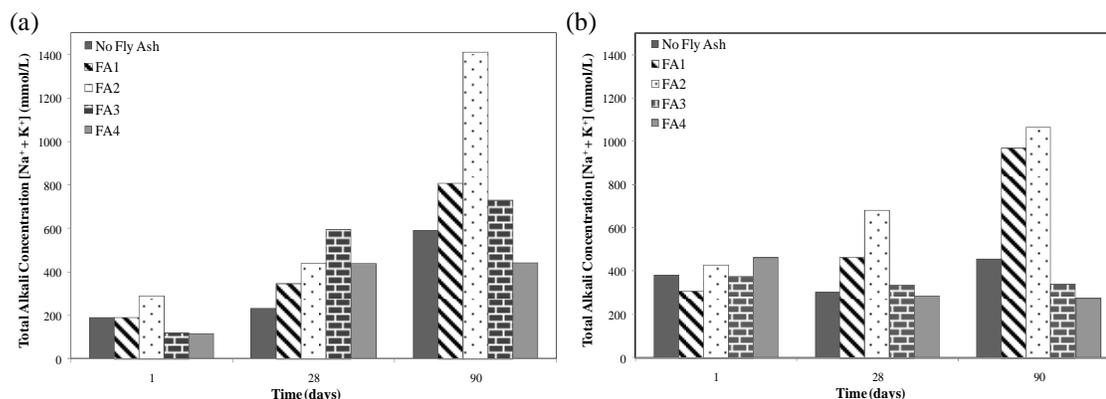
Figure 3.2. Pore solution alkali concentrations of 25% fly ash replacement levels of cement only, FA1, FA2, FA3 and FA4 with a) low alkali cement and b) high alkali cement, all cured at 38°C

Comparisons of the three replacement values (15%, 25% and 35%) of FA1 and FA3 mixed with high alkali cement and cured at 38 °C are presented in Figure 3.3. The results show that FA1, a high alkali fly ash, released significantly more alkalies over time into the pore solution than the moderate alkali FA3, despite the fact that FA3 had slightly

higher early age (1 day) values. Over the course of the 90 day testing period the alkali content of the pore solution in paste containing FA3 decreased slightly (~380 to ~346 mmol/L), indicating that alkalies from the solution were bound into the hydration products. FA1, on the other hand, continued to leach alkalies into the pore solution throughout the testing period. For both fly ashes, increasing the level of replacement resulted in decreased pore solution alkali concentrations, illustrating that increasing fly ash replacement levels enhanced alkali binding within the concrete matrix. However, FA3 was more effective at reducing pore solution alkalinity than FA1.
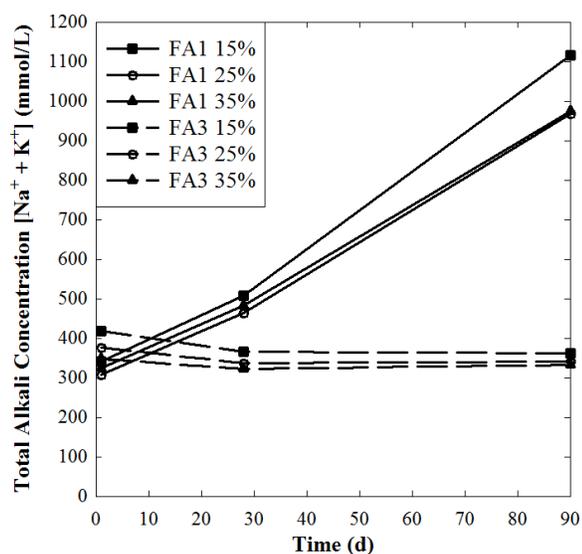
Figure 3.3. Pore solution alkali concentrations of 15%, 25%, and 35% replacements of FA1 and FA3

The temperature at which the pastes were cured had an effect on the alkali concentration of the pore solution as well. Figure 3.4 displays the temperature effects on pastes made with 25% and 35% replacement levels of FA4 and high alkali cement, cured at temperatures of either 23 ^{O}C or 60 ^{O}C for up to 90 days. FA4 is a low alkali (3.28% as Total Na_2O_{eq}) low calcium (6.16% CaO) fly ash.

Figure 3.4. Alkali concentration comparison with 25% and 35% FA4 replacements cured at 23ºC and 60ºC

As depicted in Figure 3.4, for both replacement levels the alkali concentration decreased over time. However, the samples cured at 60 °C showed decreasing alkali contents at early ages compared to the pas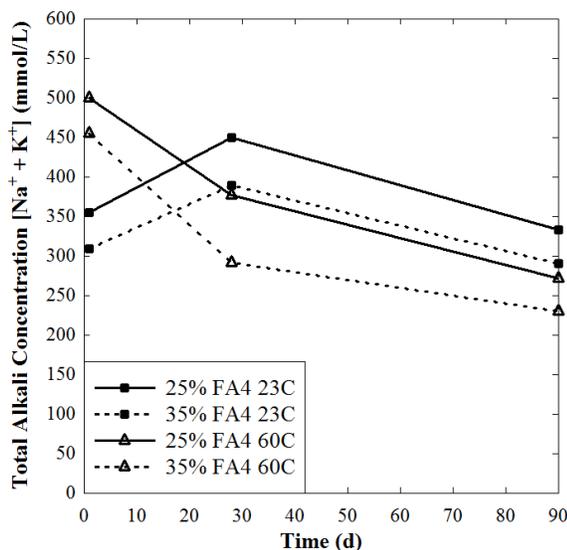te samples cured at 23 °C. The pastes cured at 23 °C showed increased pore solution alkali concentrations between days 1 and 28, before reducing considerably by 90 days. This temperature effect is anticipated to be due to acceleration of hydration at elevated temperatures, thus causing the alkalies to bind with the hydration products faster than at lower temperatures. Another trend presented in Figure 3.4 is that of consistently lower alkali concentrations in the pore solution with increased fly ash replacement levels. This trend is consistent with the results of the FA1 and FA3 as discussed previously.

Analysis of the calcium concentration of the pore solutions was also performed using ICP-OES, outlined previously. Figure 3.5a displays the comparison between the various fly ash replacement levels of FA3 and high alkali cement for samples cured at 38°C, while Figure 3.5b represents the calcium content of the raw fly ash relative to the pore solution alkalinity of paste samples made with high or low alkali cement and 25% fly ash replacement and cured for 90 days at 38 °C.
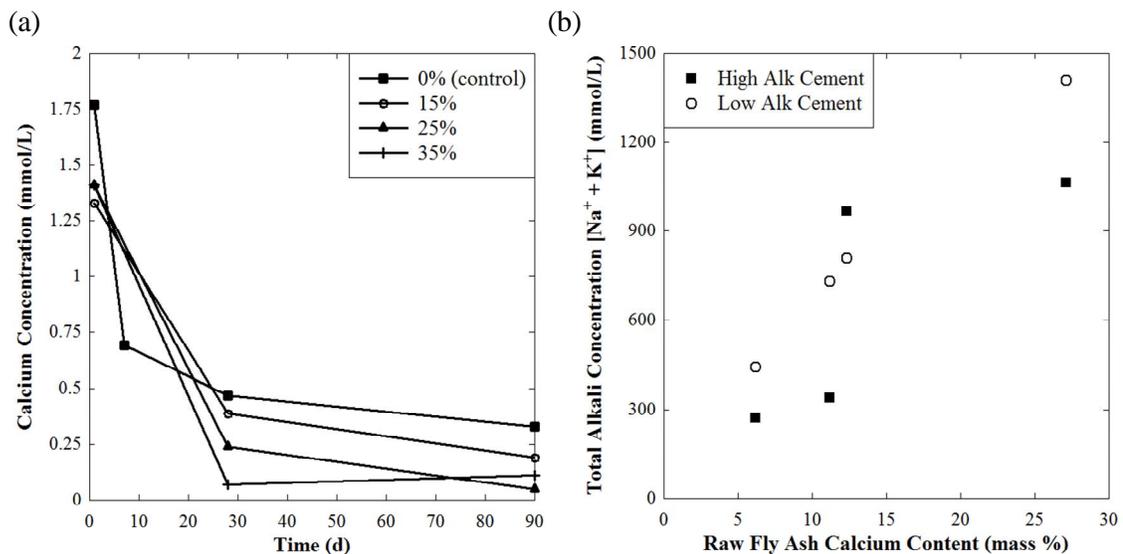
Figure 3.5. a) Calcium concentrations of paste samples cured at 38 ^{O}C with 0%, 15%, 25% and 35% Replacement levels of FA3, b) calcium content of the raw fly ash relative to the pore solution alkalinity of paste samples made with binary blends of cement and 25% fly ash replacement. All data from samples cured at 38 ^{O}C for 90 days

Overall a decrease of the pore solution calcium concentration was observed at 38 ^{O}C as the length of curing time increased. It was apparent that increasing the level of replacement of FA3 resulted in a more rapid and significant decrease of pore solution calcium concentrations. Not surprisingly, the pastes made with 0% fly ash replacements resulted in a higher concentration of calcium in the pore solution which can be attributed to the fact that the cement has a higher CaO content (63.79%) than the fly ash. Figure 3.5b illustrates that samples mixed with the high and low alkali cements resulted in a positive relationship between the raw fly ash calcium contents and the resulting pore solution alkali concentrations. An increase in the calcium ion content of the raw fly ash decreased the ability of the system to bind alkalies within the hydration products, supporting the Ca/Si ratio theory discussed previously.

A comparison was drawn between the content of free and bound alkalies. The free alkalies consisted of those leached into the pore solution, and calculations were done to determine the concentration of alkalies throughout the pore solution of the paste sample. The bound alkalies were those which absorbed into the hydration products, or the total

alkalies introduced into the system minus the free alkalies. Figure 3.6 displays this comparison of free versus bound alkalies for paste samples made with four fly ashes at 25% replacement levels of either low alkali cement (a) or high alkali cement (b) and cured at 38 ^{O}C.
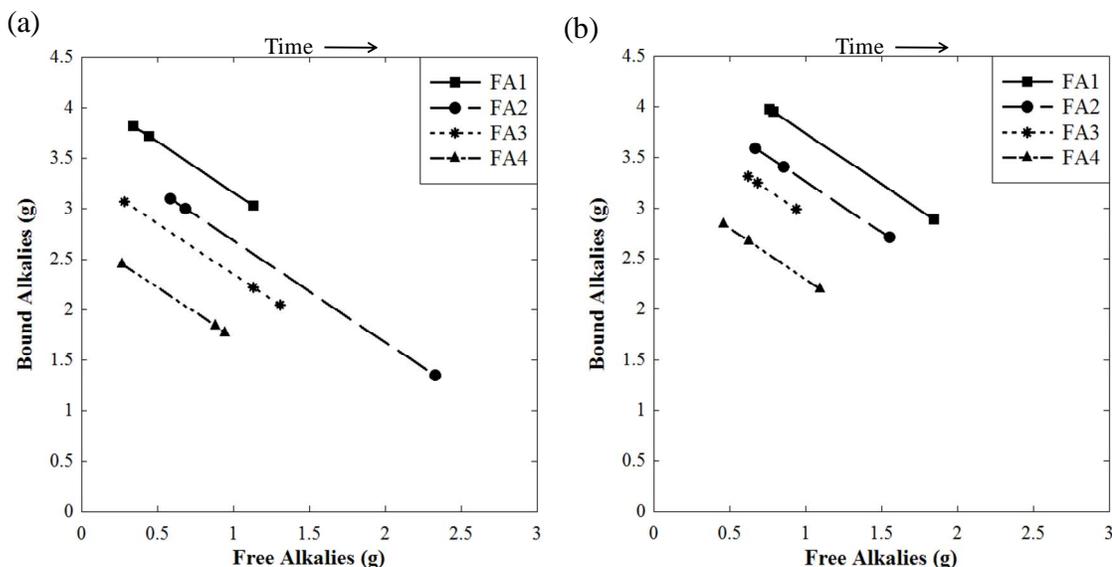
(a)

(b)

Figure 3.6. Comparison of free and bound alkalies of pastes cured at 38 ^{O}C made with 25% fly ash replacements and a) low alkali cement and b) high alkali cement

When mixed with either high or low alkali cements, the alkali content of raw fly ash significantly affected the binding abilities of the paste, as is illustrated in Figure 3.6. The highest curve represents FA1 (Total Na_2O_e 6.61%), and the isotherm curves decreased accordingly, proportionate to the total alkalies (from cement and fly ash) that were originally introduced into the sample (Total Na_2O_e for FA2: 5.60%, FA3: 4.52%, FA4: 3.28%). Each data point represents the free versus bound alkali content at a particular point in time, representing 1, 28 and 90 days moving from left to right. The space between each data point is also of importance as in pastes made with the high alkali cement (FA1 and FA2 in Figure 3.6b), it can be noted that the 1-day and 28-day alkali contents are close together, signifying that the alkalies remained bound early in the hydration process, and were not released into the pore solution until later in hydration (i.e. 90-days). The same trend can be noticed with the high alkali fly ashes (FA1 and FA2) when mixed with the low alkali cement in Figure 3.6a. However, the curves for the

moderate and low alkali fly ashes (FA3 and FA4) show that the alkalies were released early in the hydration process (28-days) and then remained stable until 90-days. Therefore, when replacing low alkali cement, moderate and low alkali fly ashes released alkalies into the pore solution in the first four weeks of hydration and then maintained the ratio of free versus bound until 90 days. This is hypothesized to be due to the hydration of the low alkali cement, which binds OH^- ions from the pore solution early, decreasing the pH of the solution and thus promoting a diffusion effect, drawing alkalies out of the hydration products and into the pore solution. Another comparison drawn from Figure 3.6 is the range of bound and free alkalies per samples made with low and high alkali cement. All samples resulted in higher bound alkali contents at early ages in pastes made with the high alkali cement than the low alkali cement. FA2, a high alkali fly ash (Total Na_2O_e 5.60%) resulted in a much lower bound alkali content after 90 days when mixed with the low alkali cement than the high alkali cement. The same trend was noticed for FA3, a moderate alkali fly ash (Total Na_2O_e 4.52%), which, with low alkali cement, released more alkalies into the pore solution later in the hydration period (28 and 90 days) in contrast to the pastes made with the high alkali cement. Figure 3.7 displays the free and bound alkalies on a percentage basis of the total alkalies introduced into the system (total alkalies from cement and fly ash).

(a)

(b)
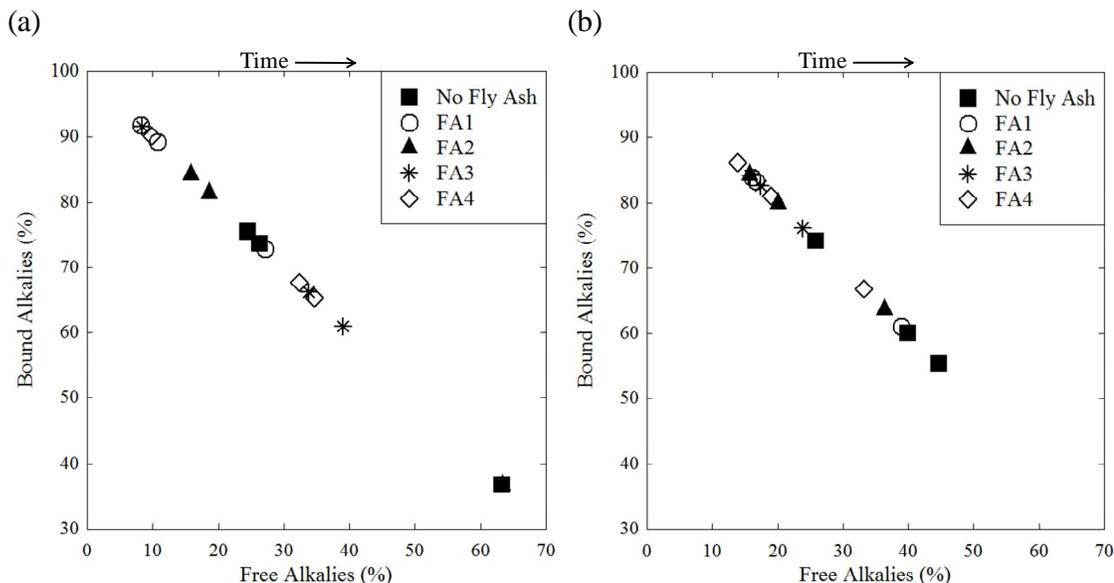
Figure 3.7. Free versus bound alkalies on a percentage basis of total alkalies put into the system (cement + fly ash total alkalies) a) with low alkali cement and b) with high alkali cement

Figure 3.7 represents the alkalies that remained bound in the hydration products versus the free alkalies available in the pore solution as a percentage of the total alkalies introduced into the system (cement + fly ash). Again it is apparent that the high alkali fly ashes (FA1 and FA2) maintained bound alkalies later in hydration whereas the mixtures with low alkali fly ash released the alkalies into the pore solution early in hydration and then remained constant. In Figure 3.7a it can be noticed that the 90 day results of the control mixture (no fly ash) and high alkali ash FA2 had significantly less bound alkalies and more free alkalies. This illustrates that these systems heavily released alkalies into the pore solution after 90 days of hydration. The fact that all the other fly ashes maintained more alkalies bound within the hydration products supports the concept that those fly ashes better bind alkalies provided by the cementitious mixture and thus released less into the pore solution. Therefore, it can be extended that those fly ashes have better ASR mitigation potential.

3.4.2 Accelerated Mortar Bar Test in Relation to Pore Solution Alkalinity

A series of ASTM C 1567 tests, (Standard Test Method for Potential Alkali Reactivity of Aggregates (mortar-bar method)) were performed on all of the listed materials to determine the effectiveness of each fly ash to mitigate ASR expansion. A thorough analysis of the results were discussed in a previous publication by the authors[1], however, Figure 3.8 displays some of the key expansion results up to 28 days for fly ashes of various chemical constituents. These results originate from ASTM C 1567 tests performed on a highly reactive aggregate with high alkali cement and 25%, 35% and 45% fly ash replacement levels.
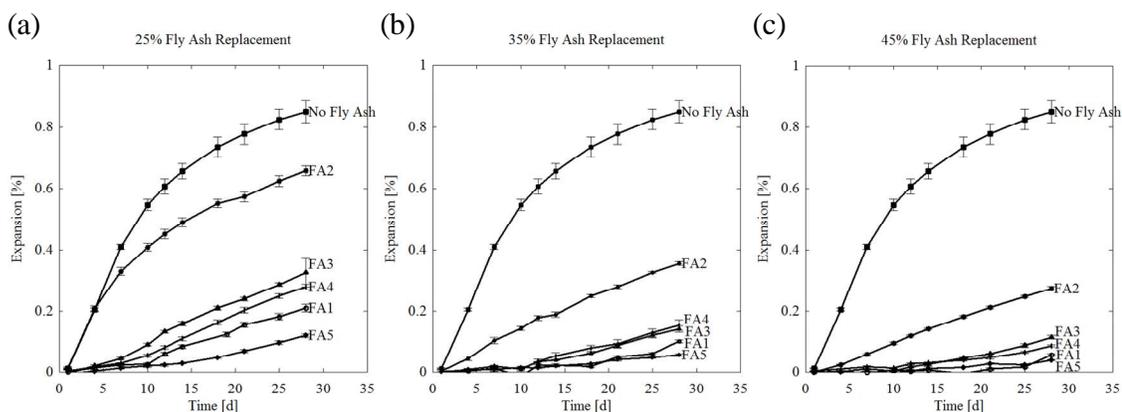
Figure 3.8. ASTM C 1567 expansion results with fly ash replacement levels of 25, 35, and 45%

Figure 3.8 displays the effectiveness of the five fly ashes used in this study to mitigate ASR expansion. The expansion results conclude that all fly ashes were effective in decreasing ASR expansion, and that effectiveness improved as the level of replacement increased. It has been discussed previously, and has been observed by other researchers, that fly ashes with a low alkali and low calcium content are better at mitigating ASR than those with higher constituents. [8, 20] This trend was observed in the results displayed in Figure 3.8, with the exception of FA1, a high alkali, moderate calcium fly ash (Total Na_2O_e 6.61%, CaO 12.3%), which, at all replacement levels was the second most successful fly ash in mitigating ASR expansion. Aside from FA1, the effectiveness of the fly ashes to control ASR increased as both the raw fly ash calcium and total alkali contents decreased, with FA2 the least successful, followed by FA3, FA4, and FA5

(Total Na$_2$O$_e$, CaO respectively: FA2 5.60%, 27.06%; FA3 4.52%, 11.16%; FA4 3.28%, 6.16%; and FA5 1.04%, 5.63%). Thus, the substantial ability of FA1 to control ASR is not attributed to the alkali or calcium content of the raw fly ash, but is presumed to be an effect of the aluminum content of the fly ash. Consequently, with increasing ability to mitigate ASR expansion, the aluminum contents of the five fly ashes also increased, as is displayed in Table 3.4.

Table 3.4. ASR expansion results in relation to raw fly ash chemical constituents

Fly Ash	28-day ASTM C 1567 Results[a]	Raw Fly Ash Constituents			Pore Solution Chemistry[b]		
		Total Na$_2$O$_e$ (mass %)	Calcium (mass %)	Aluminum (mass %)	Total Alkalies [Na$^+$ + K$^+$] (mmol/L)	Calcium (mmol/L)	Aluminum (mmol/L)
FA2	0.6585	5.60	27.06	17.04	682.83	0.14	0.47
FA3	0.3249	4.52	11.16	16.36	337.33	0.24	0.12
FA4	0.2780	3.28	6.16	16.54	283.80	0.15	0.08
FA1	0.2103	6.61	12.30	21.58	465.50	0.20	0.62
FA5	0.1207	1.04	5.63	25.14	328.29	1.22	0.19

[a]With 25% fly ash replacement
[b]Samples made with 25% fly ash replacement, cured at 38 OC for 28 days

Table 3.4 is arranged in order of decreasing 28-day expansion values and expresses the alkali, calcium and aluminum contents of the five fly ashes used as cement replacements. Again it is shown that with the exception of FA1, as the calcium and alkali contents of the raw fly ash increased, the ability of the fly ash to mitigate ASR expansion decreased. However, FA1 has the highest alkali content and second highest calcium content but proved to be the second most effective fly ash in terms of ability to control ASR. Investigating the alumina content of the raw fly ashes demonstrates that the ability to control ASR expansion increased with increasing aluminum contents, with the exception of FA2. FA2, which slightly disrupts this trend, has a significantly higher calcium content and one of the highest alkali contents, suggesting that the combination of raw constituents (high calcium, high alkali and low aluminum) is not superlative for mitigating ASR expansion. As discussed by Hong and Glasser, the contribution of aluminum ions from fly ash may saturate the hydration products resulting in a decreased Ca/Si ratio of the C-S-H, the benefits of which were discussed previously.[21] The resulting pore solution chemistry is also represented in Table 3.4. It can be noted that the total alkali content of

the pore solution also decreases as the ASTM C 1567 expansion results decrease, with the exception of FA1 and FA5. Pore solution analysis of pastes made with these fly ashes had increased levels of aluminum, suggesting that the higher raw fly ash aluminum content contributed both to the higher pore solution content and resulting ability to decrease ASR expansion. It is anticipated that the physical mineralogy of fly ash, which directly corresponds to the chemical characteristics, is a primary factor for determining the ability of an ash to control ASR. Determining where and how constituents (primarily Na^+ and K^+ and Al due to the ASR effects) are bound within the fly ash spheres would make it possible to verify how particular fly ashes will react and thus their ability to control ASR. To do this, a thorough examination of the mineralogy in conjunction with a bulk chemical analysis is necessary.

3.5   Conclusions

In an effort to better determine the alkali contribution from fly ash to the pore solutions of concrete two different procedures were performed. The first involved casting a series of cement-fly ash paste samples with varying replacement levels and types of fly ashes. All cementitious materials were chosen based on their chemical contents, with a particular focus on the alkali and calcium concentrations. The paste samples were cured for a set period at a particular temperature before the pore solution was extracted using a specialized die. After extraction the solutions were chemically analyzed to determine the sodium, potassium and calcium concentrations. Part two of this project related the pore solution chemistry determined from part one to expansion data collected from a series of ASTM C 1567 accelerated mortar bar tests. The tests were performed on samples made with varying replacement levels of the same fly ashes studied in part one and the effectiveness of the fly ashes to mitigate ASR expansion was related to the pore solution data previously collected. The following conclusions were drawn:

- The raw fly ash chemistry had a significant effect on the alkali binding capacity of the hydration products. As the alkali content of the raw fly ash increased, the resulting pore solution alkalinity did also, both in pastes made with high and low

alkali cements. Similarly, high calcium fly ashes resulted in pore solution alkalinities higher than those of low calcium fly ashes.

- Increasing the level of fly ash replacement resulted in a more rapid and significant decrease of pore solution calcium and alkali concentrations. Pastes made with 0% fly ash replacement resulted in higher concentrations of calcium in the pore solution which can be contributed to the higher CaO content of the raw cement than the raw fly ash.

- Over time, low alkali fly ashes were better able to bind alkalies contributed by the cementitious blend. After 90 days of curing the low alkali fly ash bound alkalies within the hydration products, whereas the high and moderate alkali fly ashes released alkalies into the pore solution. That said, with increasing replacement levels of moderate and high alkali fly ashes the pore solution alkali concentrations decreased, illustrating that alkali binding improves with higher replacement of these fly ashes.

- Elevating the curing temperature had a significant effect on the paste pore solution chemistry but not on the soak solution leaching analysis. At higher temperature pastes hydrated more rapidly, binding alkalies within the hydration products faster than at low temperatures.

- A relationship between the free and bound alkalies showed that low alkali fly ashes released alkalies into the pore solution earlier in hydration than high alkali fly ashes. Low alkali fly ashes released alkalies within 28 days of hydration and then maintained alkalinity until 90 days whereas high alkali ashes did not release alkalies into the pore solution until after 28 days and continued releasing alkalies through 90 days of hydration. .

- Comparing ASTM C 1567 expansion results with pore solution analysis supported the claim that the ability of fly ash to mitigate ASR decreased with increasing raw alkali and calcium contents with the exception of one fly ash. FA1, the fly ash with the highest total alkali and second highest calcium content in the study, was the second leading fly ash in controlling ASR. It is believed that

aluminum plays an important role in the ability of fly ash to mitigate ASR as this fly ash had the highest raw aluminum oxide (as Al_2O_3) content and fly ashes with decreasing aluminum contents had decreased ability to control ASR.

Recommendations for further research include a thorough analysis on the role of the fly ash aluminum content on ASR mitigation. Additionally, the mineralogy of fly ash is anticipated to have a significant effect on the ability of a given ash to control ASR. While fly ashes can be characterized by their chemical constituents, these components may be bound differently and react differently from one ash to another. Thus, research into the mineralogical organization and structure of the chemical components of fly ash would greatly enhance the understanding of how and why fly ash is able to mitigate alkali-silica reaction.

3.6 Acknowledgments

3.7 References

1. Ideker, J. and K. Schwing, *Technologies and Methodologies to Prevent Concrete Deterioration from Alkali-Silica Reaction: Testing Methods to Determine Influence of Fly Ash on Concrete Pore Solution*, L.J. Malvar, Editor. 2010, NAVFAC: Port Hueneme, CA.

2. Hasparyk, N.P., P.J.M. Monteiro, and H. Carasek, *Effect of Silica Fume and Rice Husk Ash on Alkali-Silica Reaction.* ACI Materials Journal, 2000. **97**(4): p. 486-492.

3. Folliard, K.J., et al., *Interim Recommendations for the Use of Lithium to Mitigate or Prevent Alkali-Silica Reaction (ASR).* July 2006, Federal Highway Administration.

4. Malvar, L.J. and L.R. Lenke, *Efficiency of Fly Ash in Mitigating Alkali-Silica Reaction Based on Chemical Composition.* ACI Materials Journal, 2006. **103**(5): p. 319-326.

5. Thomas, M.D.A., *Optimizing the Use of Fly Ash in Concrete*. 2007, PCA: Skokie, Illinois. p. 24.

6. Kurtis, K.E. and P.J.M. Monteiro, *Chemical additives to control expansion of alkali-silica reaction gel: proposed mechanisms of control.* Journal of Materials Science, 2003. **38**: p. 2027-2036.

7. Shehata, M.H. and M.D.A. Thomas, *Alkali Release Characteristics of Blended Cements.* Cement and Concrete Research, 2006. **36**(6): p. 1166-1175.

8. Duchesne, J. and M.A. Bérubé, *Effect of supplementary cementing materials on the composition of cement hydration products.* Advanced Cement Based Materials, 1995. **2**(2): p. 43-52.

9. Shehata, M.H. and M.D.A. Thomas, *The effects of fly ash composition on the expansion of concrete due to alkali-silica reaction.* Cement and Concrete Research, 2000. **30**: p. 1063-1072.

10. Thomas, M.D.A., et al., *Use of ternary cementitious systems containing silica fume and fly ash in concrete.* Cement and Concrete Research, 1999. **29**(8): p. 1207-1214.

11. Thomas, M. and M. Shehata. *Use of Blended Cements to Control Expansion of Concrete due to Alkali-Silica Reaction*. in *Eighth CANMET/ACI International Conference on Flyash, Silica Fume, Slag And Natural Pozzolans in Concrete*. 2004. Las Vegas, Nevada U.S.A.: ACI International.

12. Bhatty, M.S.Y. and N.R. Greening. *Interaction of alkalis with hydrating and hydrated calcium silicates*. in *Proceedings of the Fourth International Conference on the Effects of Alkalis in Cement and Concrete*. 1978. Purdue.

13. Hong, S.U. and F.P. Glasser, *Alkali binding in cement pastes: Part I. The C-S-H phase.* Cement and Concrete Research, 1999. **29**: p. 1893-1903.

14. M.D.A., T., *Discussion of the effectiveness of fly ash to mitigate ASR*, K. Schwing, Editor. 2010: Pittsburgh, PA.

15. *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, in *ASTM C 618*, A. International, Editor. 2008, ASTM International: West Conshocken, Pennsylvania. p. 3.

16. *Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency*, in *ASTM C 305*, ASTM, Editor. 2006, ASTM International: West Conshocken, PA. p. 3.

17. *Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)*, in *ASTM C1567-08*
   A. International, Editor. 2009, ASTM Int'l: West Conshohocken, Pa.

18. Kosmatka, S.H., B. Kerkhoff, and W.C. Panarese, *Design and Control of Concrete Mixtures*. 14 ed. 2008, Skokie, Illinois: Portland Cement Association.

19. Gallucci, E., P. Mathur, and K. Scrivener, *Microstructural development of early age hydration shells around cement grains.* Cement and Concrete Research, 2009. **40**: p. 4-13.

20. Shehata, M.H., M.D.A. Thomas, and R.F. Bleszynski, *The Effects of Fly Ash Composition on the Chemistry of Pore Solution in Hydrated Cement Pastes.* Cement and Concrete Research, 1999. **29**: p. 1915-1920.

21. Hong, S.U. and F.P. Glasser, *Alkali sorption by C-S-H and C-A-S-H gels Part II. Role of alumina.* Cement and Concrete Research, 2002. **32**: p. 1101-1111.

4   General Conclusion

Alkali-silica reaction is one of the leading causes of concrete deterioration worldwide and strategies to mitigate the reaction have been researched since the 1940s. The use of fly ash as a supplementary cementing material has proven to be an effective means of decreasing ASR expansion, however many challenges still exist which limit the type and amount of fly ash that can be recycled for use in concrete. One such challenge is the inability to accurately determine the alkali contribution from the fly ash to the pore solution of the concrete, which may exacerbate rather than mitigate ASR. Currently, many fly ashes are not permitted for use as an SCM because they have what is known as "borderline" alkali contents or alkali contents that are just high enough to cause concern for inducing rather than mitigating ASR. A lack of a time efficient test to determine whether or not these fly ashes have safe alkali contents is the root of the problem, and thus the result for the potentially unnecessary landfilling of fly ashe that could otherwise be recycled into concrete.

The goal of this research project, therefore, was to develop a rapid test method to accurately determine the alkali contribution from fly ash to the pore solution of concrete. Testing conducted to develop such a method included: accelerated mortar bar testing to determine the effectiveness of different fly ashes to control ASR expansion; pore solution extraction from paste samples to determine how alkalies were released into solution over time and in different curing conditions; and a leaching test to investigate the ability of the hydration products to bind and retain alkalies. In addition, a recently developed fly ash chemical index (Malvar et al. 2006), aimed to calculate the required fly ash replacement level to maintain ASR expansion to a safe level was applied and compared to experimental results determined in the lab. Two manuscripts have been compiled and were included in this thesis. The first, entitled *Influence of Alkalies from Fly Ash to Pore Solution: ASR Consideration* discussed the results of the ASTM C 1567 accelerated mortar-bar tests where it was concluded that all fly ashes used in the study effectively reduced ASR expansion, and that efficacy increased with increasing levels of fly ash

replacement. Also, the chemical index introduced by Malvar and coworkers was applied to the materials tested in this project and it was determined that the index is sufficient for low calcium and low alkali fly ashes, but is not suitable for fly ashes with moderate or high alkali and calcium contents. The second manuscript, *Fly Ash and the Mitigation of Alkali-Silica Reaction: Alkali Availability*, presents the results of pore solution extraction and analysis from cement-fly ash paste samples and compares the pore solution results with the ASTM C 1567 testing. It was concluded that fly ashes with higher total alkali contents do tend to release more alkalies into the pore solution, and they do so faster at elevated temperatures. The comparison between the accelerated mortar bar test and the pore solution analysis verified that the use of fly ash successfully decreased ASR expansion, and more so with increasing replacement levels. It was proposed that alumina plays a vital role in the ability of a fly ash to mitigation the ASR reaction and this is an area for future work.

Although a test method was not fully developed, the research performed and discussed in this document provides much of the preliminary work necessary to do so. Further analysis of the binding characteristics of fly ash alkalies into the hydration products over time (i.e. beyond 90 days) is necessary in order to make a sufficient and accurate test. In addition, Malvar et al.'s chemical index has promise for determining the fly ash replacement level needed to control expansion to a safe level, however, modifications are necessary to include all applicable fly ashes. Further investigation into these issues is suggested for future research.

BIBLIOGRAPHY

1. Ideker, J., *Crack in concrete slab caused by Alkali-Silica Reaction*, K. Schwing, Editor. 2009: Corvallis.
2. Kurtis, K., *Portland Cement Hydration*. 2007, School of Civil Engineering, Georgia Institute of Technology: Atlanta, Georgia. p. 35.
3. Stanton, T.E., *Expansion of Concrete Through Reaction Between Cement and Aggregate*. American Society of Civil Engineers, 1940. 66: p. 1781-1811.
4. Folliard, K.J., et al., *Interim Recommendations for the Use of Lithium to Mitigate or Prevent Alkali-Silica Reaction (ASR)*. July 2006, Federal Highway Administration.
5. Mehta, P.K. and P.J.M. Monteiro, *Concrete: Microstructure, Properties, and Materials*. 3 ed. 2006, New York: McGraw-Hill.
6. Pedneault, A., *Development of Testing and Analytical Procedures for teh Evaluation of the Residual Potential of Reaction, Expansion, and Deterioration of Concrete Affected by ASR*. 1996, Laval University: Quebec City, Canada. p. 133.
7. Thomas, M.D.A., *The Role of Calcium in Alkali-Silica Reaction*. Materials Science of Concrete - The Sidney Diamond Symposium, 2002: p. 325-331.
8. Hansen, W.C., *Studies Relating to the Mechanism by Which the Alkali-Silica Reaction Proceeds in Concrete*. Journal of the American Concrete Institute, 1944. 15(3): p. 213-27.
9. Wang, H. and J.E. Gillott, *Mechanism of Alkali-Silica Reaction and the Significance of Calcium Hydroxide*. Cement and Concrete Research, 1991. 21(4): p. 647-654.
10. Chatterji, S., *The Role of Ca(OH)$_2$ in the Breakdown of Portland Cement Concrete due to Alkali-Silica Reaction*. Cement and Concrete Research, 1979. 9(2): p. 185-188.
11. Chatterji, S. and N.F. Clausson-Kass, *Prevention of Alkali-Silica Expansion by Using Slag-Portland Cement*. Cement and Concrete Research, 1984. 14(6): p. 816-818.
12. Diamond, S. *ASR −Another Look at Mechanisms*. in *Proceedings of the 8th International Conference on Alkali-Aggregate Reaction*. 1989. Kyoto.
13. Thomas, M.D.A., P.J. Nixon, and K. Pettifer. *Effect of Pulverised-Fuel Ash With a High Total Alkali Content on Alkali Silica Reaction in Concrete Containing Natural UK Aggregate*. in *Proceedings of the 2nd CANMET/ACI International Conference on Durability of Concrete* 1991. Detroit: American Concrete Institute.
14. Bleszynski, R.F. and M.D.A. Thomas, *Microstructural Studies of Alkali-silica Reaction in Fly Ash Concrete Immersed in Alkaline Solutions*. Advanced Cement Based Materials, 1998. 7: p. 66-78.
15. Hansen, W.C., *Studies Relating to the Mechanism by Which the Alkali-Silica Reaction Proceeds in Concrete*. Journal of the American Concrete Institute, 1944. 15: p. 213-227.
16. Chatterji, S., Thalow, N., Jensen, A.D., *Studies of the Alkali-Silica Reaction, Part 4: Effect of Different Alkali Salt Solutions on Expansion*. Cement and Concrete Research, 1987. 17: p. 777-783.
17. Rotter, H.M., *Alkali-aggregateReaction: From Basic Principles to Structural Behavior - Literature Review*. 1995, Department of Civil Engineering, École Polytechnique de Montréal: Montréal, PQ.
18. Prezzi, M., P.J.M. Monteiro, and G. Sposito, *The Alkali-Silica Reaction, Part I: Use of the Double-Layer Theory to Explain the Behavior of Reaction-Product Gels*. ACI Materials Journal, 1997. January-February 1997(Title no.94-M2): p. 10-17.
19. *Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)*, in *ASTM C 1260*. 2007, ASTM International: West Conshohocken, PA. p. 5.

20.   Thomas, M.D.A., et al., *Performance Limits for Evaluating Supplementary Cementing Materials using the Accelerated Mortar Bar Test.* PCA R&D Serial No. 2892, 2005: p. 1-22.

21.   *Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)*, in *ASTM C 1567*. 2008, ASTM International: West Conshohocken, PA. p. 6.

22.   Leemann, A., B. Lothenbach, and C. Thalmann, *Influence of superplasticizers on pore solution composition and on expansion of concrete due to alkali-silica reaction.* Construction and Building Materials, 2011. 25(1): p. 344-350.

23.   *Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction*, in *ASTM C 1293-08b*, A. International, Editor. 2008, ASTM International: West Conshohocken, PA. p. 7.

24.   *Standard Practice for Laboratory Testing to Demonstrate the Effectiveness of Supplementary Cementing Materials and Lithium-based Admixtures to Prevent Alkali-silica Reaction in Concrete*, in *A23.2-28A*. 2004b, Canadian Standards Association: Mississauga, ON, CA. p. 327-330.

25.   *Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction*, in *ASTM C 1293-08*. 2008, ASTM International: West Conshohocken, PA. p. 6.

26.   *Standard Practice for Petrographic Examination of Hardened Concrete*, in *ASTM C856-04*, ASTM, Editor. 2004, ASTM International: West Conshohocken, Pa. p. 17.

27.   Guthrie, G.D. and J.W. Carey, *Geochemical Methods for the Identification of ASR Gel.* 1998, Los Alamos National Laboratory: Los Alamos, NM. p. 13.

28.   USACE, *Unified Facilities Guide Specifications*, in *UFGS-32 13 11*, USACE, Editor. 2007.

29.   Malvar, L.J., *ASR guidelines in DOD Unified Facilities Guide Specifications*. 2009, NAVFAC ESC: Port Hueneme, CA.

30.   Tremblay, C., et al., *Experimental investigation of the mechanisms by which LiNO3 is effective against ASR.* Cement and Concrete Research, 2010. 40(4): p. 583-597.

31.   Tremblay, C., et al., *Effectiveness of Lithium-Based Products in Concrete Made with Canadian Natural Aggregates Susceptible to Alkali- Silica Reactivity.* ACI Materials Journal, 2007. 104(2): p. 195-205.

32.   Stark, D. *Lithium Salt Admixtures - An Alternative Method to Prevent Expansive Alkali-Silica Reactivity*. in *Ninth International Conference on Alkali-Aggregate Reaction in Concrete*. 1992. London, United Kingdom.

33.   Barborak, R., *Using Lithium Compounds as an Admixture in New Concrete and as a Posttreatment for Exisiting Concrete Affected by Alkali-silica Reaction*, in *Department of Civil, Architectural and Environmental Engineering*. 2005, The University of Texas at Austin: Austin, Texas.

34.   Kosmatka, S.H., B. Kerkhoff, and W.C. Panarese, *Design and Control of Concrete Mixtures*. 14 ed. 2008, Skokie, Illinois: Portland Cement Association.

35.   Mehta, P.K. and K.J. Folliard. *Rice Husk Ash-A Unique Supplementary Cementing Material*. in *Proceedings of teh International Symposium on Advances in Concrete Technology*. 1992.

36.   Siddique, R. and J. Klaus, *Influence of metakaolin on the properties of mortar and concrete: A review.* Applied Clay Science, 2009. 43(3-4): p. 392-400.

37.   Zhang, M.H., R. Lastra, and V.M. Malhotra, *Rice-husk ash paste and concrete: Some aspects of hydration and the microstructure of the interfacial zone between the aggregate and paste.* Cement and Concrete Research, 1996. 26(6): p. 963-977.

38.   Dong, D.V., P.D. Huu, and N.N. Lan. *Effect of Rice Husk Ash on Properties of High Strength Concrete*. in *The 3rd ACF International Conference - ACF/VCA 2008*. 2008.

39.   Ramezanianpour, A.A., K. Zarrabi, and M. Mahdikhani, *Mitigation of Alkali Aggregate Reaction of Concrete Incorporation Rice Husk Ash (RHA)*, Department of Civil Engineering, Amirkabir University of Technology: Tehran, Iran.

40.   Multon, S., et al., *Effects of aggregate size and alkali content on ASR expansion.* Cement and Concrete Research, 2010. 40(4): p. 508-516.

41.   318, A.C., *Structural Building Code*, in *ACI Committee 318, ACI 318*, ACI, Editor. 2008, ACI: Farmington Hills, Michigan.

42.   Thomas, M.D.A., *Optimizing the Use of Fly Ash in Concrete*. 2007, PCA: Skokie, Illinois. p. 24.

43.   Daderko, G., *Concrete Failures...and How SCMs Can Help Prevent Them.* The Construction Specifier, 2008: p. 26-38.

44.   Mehta, P.K. and P.J.M. Monteiro, *Concrete: Microstructure, Properties, and Materials*. 3 ed. 2006, New York: McGraw-Hill. 659.

45.   Association, A.C.A. *Advancing the Management and use of Coal Combustion Products*. 2009 [cited 2009 May 7]; Available from: http://www.acaa-usa.org/.

46.   *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, in *ASTM C 618*, A. International, Editor. 2008, ASTM International: West Conshocken, Pennsylvania. p. 3.

47.   Glasser, F.P., ed. *Chemistry of the Alkali-Aggregate Reaction*. The Alkali-Silica Reaction in Concrete, ed. R.N. Swamy. 1992: Blackie, London, United Kingdom. 96-121.

48.   Headwaters, *Fly Ash for Concrete*, H. Resources, Editor. 2005: South Jordan, Utah.

49.   Mehta, K.P. *High-Performance, High-Volume Fly Ash Concrete for Sustainable Development*. in *International Workshop on Sustainable Development and Concrete Technology*. 2004. Beijing, China.

50.   Duchesne, J. and M.A. Be´rube´, *Effect of supplementary cementing materials on the composition of cement hydration products.* Advanced Cement Based Materials, 1995. 2(2): p. 43-52.

51.   Shehata, M.H. and M.D.A. Thomas, *Alkali Release Characteristics of Blended Cements.* Cement and Concrete Research, 2006. 36(6): p. 1166-1175.

52.   Shehata, M.H., M.D.A. Thomas, and R.F. Bleszynski, *The Effects of Fly Ash Composition on the Chemistry of Pore Solution in Hydrated Cement Pastes.* Cement and Concrete Research, 1999. 29: p. 1915-1920.

53.   Diamond, S., *Effects of two Danish fly ashes on alkali contents of pore solutions of cement fly ash pastes.* Cement and Concrete Research, 1981. 11(3): p. 383-94.

54.   Malvar, L.J. and L.R. Lenke, *Efficiency of Fly Ash in Mitigating Alkali-Silica Reaction Based on Chemical Composition.* ACI Materials Journal, 2006. 103(5): p. 319-326.

55.   AACA, *Fly Ash Facts for Highway Engineers*, in *Federal Highway Administration Report FHWA-SA-94-081*. 1995, American Coal Ash Association: Washington, D.C. p. 70.

56.   NMDOT, *Supplement to the 2000 Edition of the Standard Specifications for Highway and Bridge Construction*, N.M.D.o. Transportation, Editor. 2004.

57.   Malvar, L.J., et al., *Closure to Discussion of "Alkali Silica Reaction Mitigation: State-of-the-Art and Recommendations".* ACI Materials Journal, 2003. 100(4): p. 346-350.

58. Mehta, P.K. *Standard Specifications for Mineral Admixtures - An Overview*. in *Proceedings of Second CANMET/ACI International Conference*. 1986. Farmington Hills, Mich.

59. *ASTM C618 Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, in *ASTM C618-09*, A. International, Editor. 2009, ASTM International: West Conshohocken, PA.

60. Klieger, P. and S. Gebler. *Fly Ash and Concrete Durability*. in *Concrete Durability: Katharine and Bryant Mather International Conference*. 1987. Farmington Hills, Mich: American Concrete Institute.

61. Malhotra, V.M. and A.A. Ramezanianpour, *Fly Ash in Concrete*, in *Canada Center for Mineral and Energy Technology, Natural Resources Canada,* , CANMET, Editor. 1994, MSL 94-45(IR): Ottawa, Ontario, Canada. p. 307.

62. Thomas, M. and M. Shehata, *Use of Blended Cements to Control Expansion of Concrete due to Alkali-Silica Reaction*, in *Eighth CANMET/ACI International Conference on Flyash, Silica Fume, Slag And Natural Pozzolans in Concrete*, P. Gupta, Editor. 2004: Las Vegas, U.S.A. p. 591-607.

63. ASTM, *Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete*, in *ASTM C311*. 2007, ASTM International: West Conshohocken, PA.

64. Thomas, M., et al., *Test methods for evaluating preventive measures for controlling expansion due to alkali-silica reaction in concrete*. Cement and Concrete Research, 2006. 36: p. 1842-1856.

65. Headwaters. *Fly Ash and the Environment*. 2010 [cited 2010 October 20, 2010]; Available from: http://www.flyash.com/flyashenvironment.asp.

66. Ideker, J. and K. Schwing, *Technologies and Methodologies to Prevent Concrete Deterioration from Alkali-Silica Reaction: Testing Methods to Determine Influence of Fly Ash on Concrete Pore Solution*, L.J. Malvar, Editor. 2010, NAVFAC: Port Hueneme, CA.

67. Hasparyk, N.P., P.J.M. Monteiro, and H. Carasek, *Effect of Silica Fume and Rice Husk Ash on Alkali-Silica Reaction*. ACI Materials Journal, 2000. 97(4): p. 486-492.

68. Kurtis, K.E. and P.J.M. Monteiro, *Chemical additives to control expansion of alkali-silica reaction gel: proposed mechanisms of control*. Journal of Materials Science, 2003. 38: p. 2027-2036.

69. Shehata, M.H. and M.D.A. Thomas, *The effects of fly ash composition on the expansion of concrete due to alkali-silica reaction*. Cement and Concrete Research, 2000. 30: p. 1063-1072.

70. Thomas, M.D.A., et al., *Use of ternary cementitious systems containing silica fume and fly ash in concrete*. Cement and Concrete Research, 1999. 29(8): p. 1207-1214.

71. Bhatty, M.S.Y. and N.R. Greening. *Interaction of alkalis with hydrating and hydrated calcium silicates*. in *Proceedings of the Fourth International Conference on the Effects of Alkalis in Cement and Concrete*. 1978. Purdue.

72. Hong, S.U. and F.P. Glasser, *Alkali binding in cement pastes: Part I. The C-S-H phase*. Cement and Concrete Research, 1999. 29: p. 1893-1903.

73. Thomas, M.D.A., *Review of the effect of fly ash and slag on alkali-aggregate reaction in concrete*. 1996, Construction Research Communications: Watford (U.K.). p. 117.

74. Kollek, J.J., S.P. Varma, and C. Zaris. *Measurement of OH⁻ concentrations of pore fluids and expansion due to alkali-silica reaction in composite cement mortars*. in *Proceedings of the 8th International Congress on the Chemistry of Cemetn*. 1986. Rio de Janeiro.

75.   *Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency*, in *ASTM C 305*, ASTM, Editor. 2006, ASTM International: West Conshocken, PA. p. 3.

76.   *Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)*, in *ASTM C1567-08*
        A. International, Editor. 2009, ASTM Int'l: West Conshohocken, Pa.

77.   Gallucci, E., P. Mathur, and K. Scrivener, *Microstructural development of early age hydration shells around cement grains.* Cement and Concrete Research, 2009. 40: p. 4-13.

78.   Hong, S.U. and F.P. Glasser, *Alkali sorption by C-S-H and C-A-S-H gels Part II. Role of alumina.* Cement and Concrete Research, 2002. 32: p. 1101-1111.

79.   Taylor, H.F.W., *A method for predicting alkali ion concentrations in cement pore solutions.* Advances in Cement Research 1987. 1: p. 5-16.

80.   Chen, W. and H.J.H. Brouwers, *Alkali binding in hydrated Portland cement paste.* Cement and Concrete Research, 2009. 40: p. 716-722.

81.   Thomas, M.D.A. and F.A. Innis, *Use of the Accelerated Mortar Bar Test for Evaluating the Efficacy of Mineral Admixtures for Controlling Expansion due to Alkali-Silica Reaction.* Cement, Concrete, and Aggregates, 1999. 21: p. 157-164.

82.   *Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)*, in *ASTM C1260-07*, A. International, Editor. 2009, ASTM International West Conshohocken, PA.

83.   ACI, C., *State-of-the-Art Report on Alkali-Aggregate Reactivity (221.1R-98).* 1998, American Concrete Institute: Farmington Hills, Mich. p. 31.

84.   Malvar, L.J., et al., *Alkali-Silica Reation Mitigation: State of the Art and Recommendations.* ACI Materials Journal, 2002. 99(No. 5): p. 480-489.

85.   *Concrete Pavement for Airfields and Other Heavy-Duty Pavements more than 10,000 Cubic Yards*, in *Specification 32 13 11*, Unified Facilities Guide, Editor. 2009.

APPENDICES

Appendix A

ASTM C 1567 Results
Aggregate 1
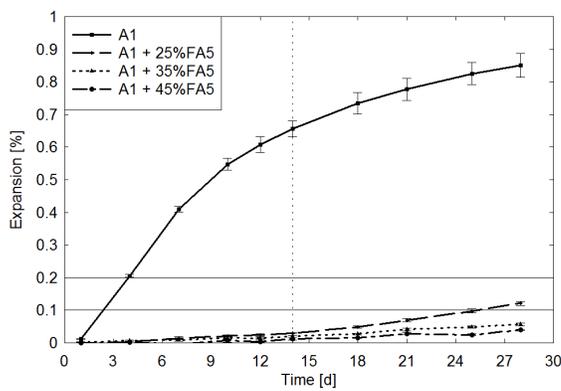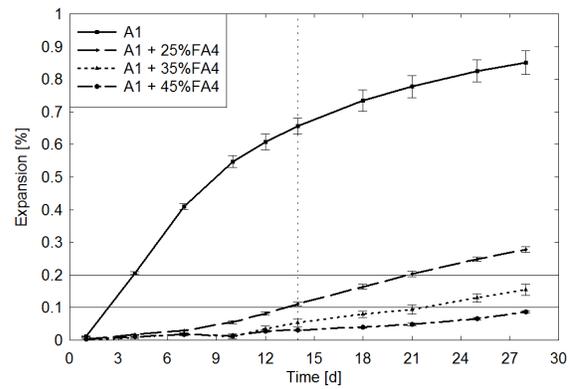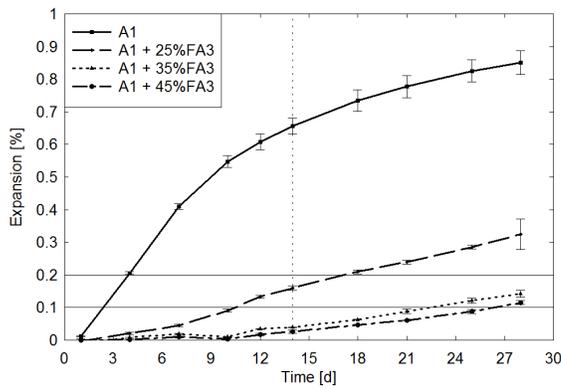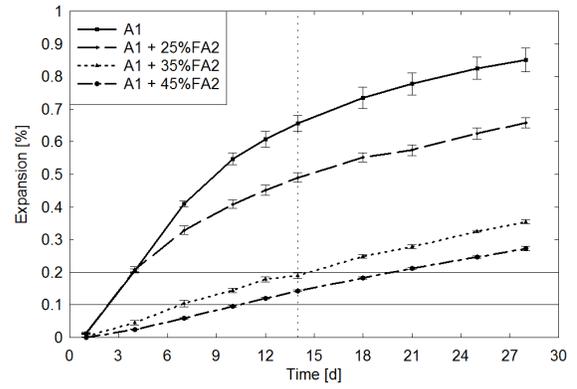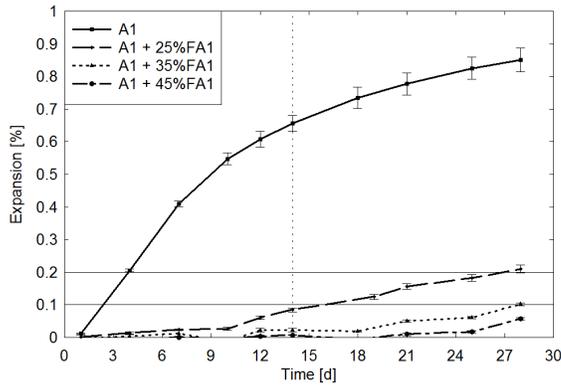
Aggregate 2
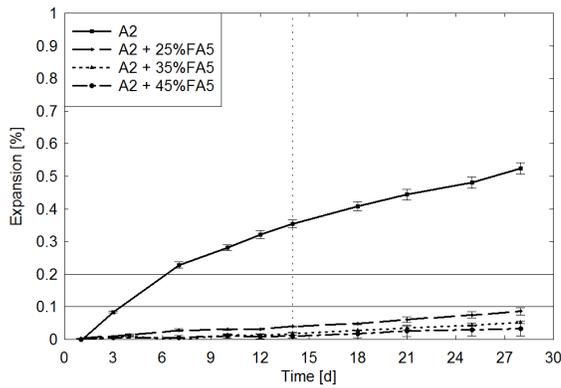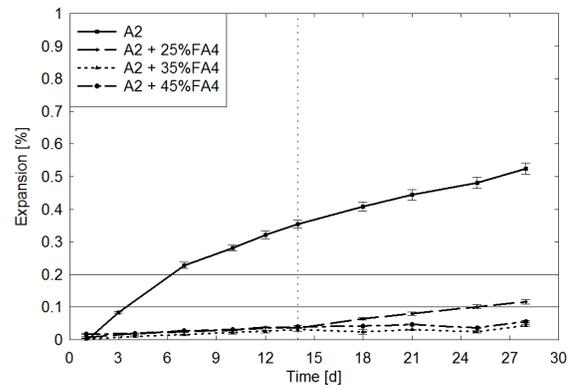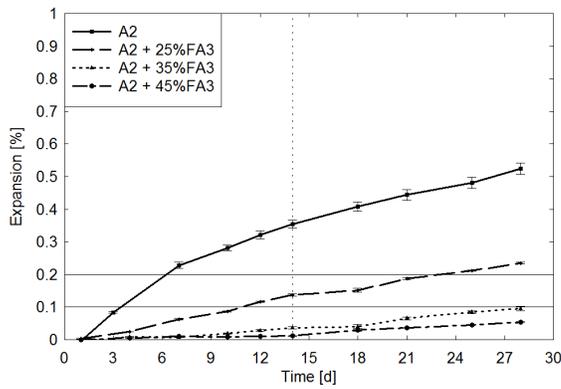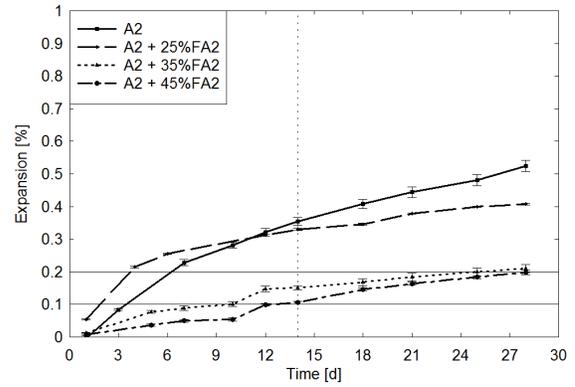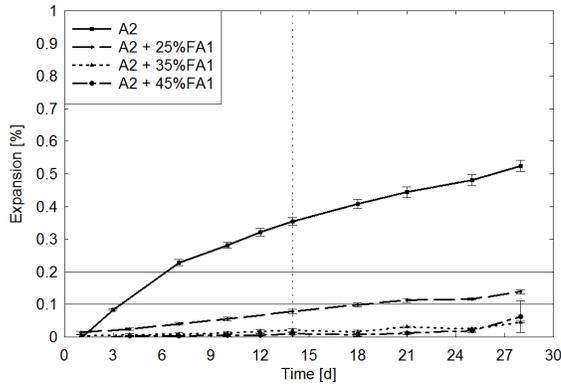
Aggregate 3
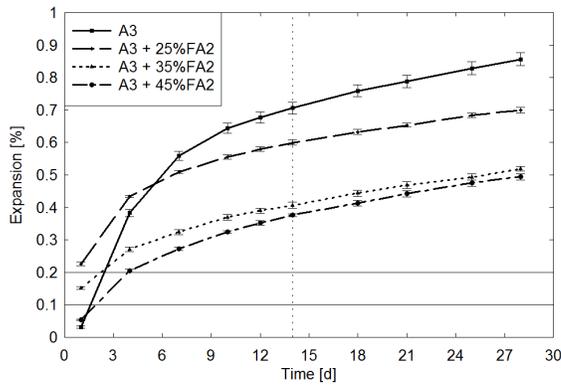
Chemical Index

Predicted replacement levels to maintain expansion below 0.08%

Fly Ashes		Predicted replacement levels to maintain expansion <0.08% based on experimental data	
		A1 aggregate	A2 aggregate
FA1	Mean	20.8	18.9
	95% Low	14.2	6.8
	95% High	27.5	31.1
FA2	Mean	58.7	45.2
	95% Low	12.1	-11.2
	95% High	105.3	101.7
FA3	Mean	29.2	23.3
	95% Low	18.8	5.3
	95% High	39.6	41.3
FA4	Mean	29.9	21.3
	95% Low	27.8	-3.3
	95% High	32.1	45.9

Appendix B

Table 1: Pore solution ICP results for all fly ash-cement paste samples

Sample	Temperature (^{O}C)	Time (days)	Low Alkali Cement			High Alkali Cement		
			Alkalies [Na$^+$ + K$^+$] (mmol/L)	Calcium (mmol/L)	Aluminum (mmol/L)	Alkalies [Na$^+$ + K$^+$] (mmol/L)	Calcium (mmol/L)	Aluminum (mmol/L)
Control (0%)	23	1	142.38	1.98	0.00	0.40	0.49	0.03
		28	506.58	2.27	0.07	0.46	0.45	0.04
		90	594.41	0.98	0.24	0.56	0.29	0.04
	38	1	188.91	1.52	0.00	0.38	1.77	0.10
		28	231.95	1.01	0.00	0.30	0.47	0.17
		90	590.12	1.81	0.07	0.45	0.33	0.05
	60	1	210.70	1.23	0.00	0.33	0.79	0.08
		28	201.68	0.58	0.01	0.47	0.32	0.01
		90	609.54	2.41	0.12	0.39	0.87	0.00
FA1 (15%)	23	1				0.30	0.89	0.00
		28				0.56	0.23	0.34
		90				0.98	1.17	0.36
	38	1				0.34	0.61	0.06
		28				0.51	0.00	2.19
		90				1.12	0.40	4.20
	60	1				0.42	0.65	0.00
		28				0.55	0.21	0.96
		90				1.32	1.37	0.57
FA1 (25%)	23	1	145.34	1.76	0.00	0.27	0.75	0.00
		28	261.29	0.92	0.00	0.41	0.53	0.00
		90	806.21	0.67	0.77	1.03	0.67	1.09
	38	1	188.62	1.2	0.00	0.31	0.65	0.00
		28	344.34	0.28	0.48	0.47	0.20	0.62
		90	810.03	0.66	1.09	0.97	0.44	2.13
	60	1	321.16	0.47	0.06	0.39	0.12	0.10
		28	396.01	0.41	0.37	0.44	0.11	0.43
		90	1179.51	1.17	0.54	1.17	0.58	0.90
FA1 (35%)	23	1				0.24	0.88	0.00
		28				0.42	0.32	0.14
		90				0.94	0.45	2.37
	38	1				0.32	0.57	0.08
		28				0.48	0.09	1.47
		90				0.98	0.30	3.83
	60	1				0.37	0.00	0.59
		28				0.43	0.07	0.95
		90				1.00	0.44	2.26
FA2 (15%)	23	1				353.37	0.46	0.09
		28				507.08	0.53	0.00
		90				1035.25	0.19	0.12
	38	1				415.18	0.53	0.64
		28				1001.13	0.00	0.84
		90				967.12	0.48	0.10
	60	1				497.14	0.60	0.24
		28				485.28	0.80	0.11
		90				739.17	0.90	0.07

Mix	Temp	Age						
FA2 (25%)	23	1	196.63	0.96	0.00	400.00	0.34	0.23
		28	378.54	1.07	0.06	664.29	0.39	0.66
		90	1369.59	1.76	0.25	1311.31	0.04	0.12
	38	1	288.94	0.74	0.00	430.97	0.20	0.08
		28	439.18	0.57	0.12	682.83	0.14	0.47
		90	1412.05	0.52	0.15	1066.18	0.31	0.31
	60	1	393.01	0.64	0.00	546.17	0.21	0.36
		28	527.79	0.66	0.10	1245.78	0.06	0.14
		90	1527.45	1.06	0.00	1684.88	0.79	0.41
FA2 (35%)	23	1				438.41	0.91	0.16
		28				708.34	0.13	0.95
		90				1441.66	0.03	0.62
	38	1				549.95	0.45	0.44
		28				590.72	0.07	1.04
		90				630.64	0.20	0.43
	60	1				554.68	0.15	0.48
		28				1199.43	0.05	0.29
		90				672.20	0.38	0.39
FA3 (15%)	23	1				388.46	1.50	0.00
		28				335.91	0.81	0.00
		90				381.78	0.66	0.00
	38	1				418.07	1.33	0.00
		28				365.67	0.39	0.11
		90				363.32	0.19	0.04
	60	1				513.85	1.21	0.00
		28				378.24	0.41	0.00
		90				908.92	1.14	0.00
FA3 (25%)	23	1	94.04	1.92	0.00	332.59	1.38	0.00
		28	487.29	1.97	0.22	315.05	0.82	0.02
		90	696.84	1.44	1.31	323.76	0.31	0.00
	38	1	116.79	1.60	0.00	377.05	1.41	0.00
		28	595.19	0.69	0.46	337.33	0.24	0.12
		90	731.08	0.67	0.44	341.49	0.05	0.15
	60	1	205.96	0.71	0.00	513.37	0.77	0.02
		28	665.59	1.07	0.28	397.74	0.35	0.10
		90	883.71	1.20	1.22	480.56	0.30	0.00
FA3 (35%)	23	1				310.07	1.67	0.00
		28				271.13	0.64	0.02
		90				286.78	0.12	0.05
	38	1				347.54	1.41	0.00
		28				322.16	0.07	0.55
		90				333.29	0.11	0.59
	60	1				475.51	0.44	0.32
		28				312.89	0.04	0.27
		90				400.67	0.26	0.00
FA4 (25%)	23	1	94.77	2.02	0.03	354.88	0.45	0.00
		28	416.26	2.50	0.00	449.90	1.09	0.04
		90	566.24	1.33	0.00	333.50	0.17	0.12
	38	1	114.47	1.72	0.00	461.42	0.74	0.06
		28	439.32	0.70	0.18	283.80	0.15	0.08
		90	441.55	0.87	0.23	272.85	0.21	0.25
	60	1	164.47	0.72	0.00	499.79	0.22	0.02
		28	549.76	1.05	0.22	376.65	0.48	0.21
		90	497.60	1.38	0.07	272.08	0.34	0.00

Mix	Cure and Soak Temperature	Soak Time (days)			
		1	308.87	0.49	0.00
	23	28	389.35	0.86	0.05
		90	290.42	0.15	0.13
FA4 (35%)		1	229.63	0.55	0.01
	38	28	268.65	0.22	0.54
		90	490.58	0.45	1.18
		1	454.70	0.22	0.01
	60	28	291.84	0.28	0.44
		90	230.55	0.29	0.00

Table 2: Soak solution chemical analysis for all fly ash-paste samples

Mix	Cure and Soak Temperature	Soak Time (days)	Soak Solution Concentration (mol/L)	Alkalies [$Na^+ + K^+$] (mmol/L)
0%	23 °C	14	0	11.06
			0.3	201.29
			0.5	329.66
			0.7	472.77
			1	674.40
		28	0	16.16
			0.3	277.82
			0.5	457.96
			0.7	649.79
			1	944.12
	38 °C	14	0	13.23
			0.3	190.87
			0.5	319.83
			0.7	462.14
			1	671.34
		28	0	19.17
			0.3	271.90
			0.5	451.93
			0.7	636.56
			1	906.20
FA1 15%	23 °C	14	0	16.72
			0.3	277.01
			0.5	480.84
			0.7	670.87
			1	957.82
		28	0	26.47
			0.3	394.44
			0.5	666.19
			0.7	925.54
			1	1352.95
	38 °C	14	0	20.67
			0.3	288.11
			0.5	483.11
			0.7	674.58
			1	972.86
		28	0	27.91
			0.3	390.75
			0.5	666.15
			0.7	948.71
			1	1329.63

FA1 35%	23 °C	14	0	22.40
			0.3	276.33
			0.5	462.99
			0.7	641.95
			1	905.03
		28	0	31.08
			0.3	385.73
			0.5	648.73
			0.7	899.67
			1	1258.13
FA1 35%	38 °C	14	0	26.67
			0.3	279.12
			0.5	468.11
			0.7	646.28
			1	922.64
		28	0	39.46
			0.3	382.06
			0.5	647.19
			0.7	865.75
			1	1255.63
FA5 15%	23 °C	14	0	12.16
			0.3	277.24
			0.5	474.14
			0.7	676.88
			1	944.09
		28	0	13.15
			0.3	420.05
			0.5	730.58
			0.7	1002.41
			1	1457.18
	38 °C	14	0	12.63
			0.3	275.00
			0.5	473.67
			0.7	667.28
			1	959.95
		28	0	16.28
			0.3	328.97
			0.5	677.15
			0.7	638.79
			1	792.76
FA5 35%	23 °C	14	0	10.36
			0.3	283.17
			0.5	465.17
			0.7	661.35
			1	970.33
		28	0	28.81
			0.3	248.08
			0.5	234.63
			0.7	758.08
			1	1083.67
FA5 35%	38 °C	14	0	10.28
			0.3	279.76
			0.5	469.08
			0.7	666.03

			1	964.60
FA5 35%	38 ^{O}C	28	0	37.38
			0.3	400.12
			0.5	706.32
			0.7	991.50
			1	1452.97