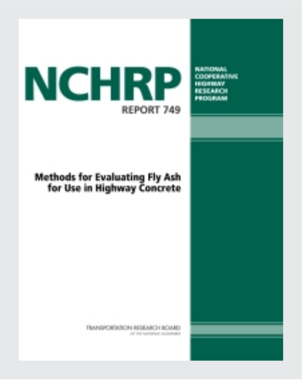

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NATIONAL COOPERATIVE HIGHWAY RESEARCH PROGRAM

NCHRP REPORT 749

Methods for Evaluating Fly Ash for Use in Highway Concrete

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Dr. Lawrence Sutter, professor and director of the Michigan Tech Transportation Institute, was the Principal Investigator. The other authors of this report were Dr. R. Douglas Hooton, P.E., Professor of Civil Engineering at the University of Toronto and Co-principal Investigator, and Dr. Scott Schlorholtz, Adjunct Assistant Professor of Civil, Construction and Environmental Engineering at Iowa State University and Co-principal investigator. Other contributors to the research were Dr. David Hand, P.E., Professor of Civil and Environmental Engineering at MTU; Dr. Karl Peterson, Assistant Professor of Civil Engineering at the University of Toronto; Melanie Kueber, P.E., Ph.D. student at MTU; Zeyad Ahmed, P.E., Ph.D. student at MTU; Andre de Groot, M.S. student at the University of Toronto; and Benjamin Longmire, B.S. student at MTU. The work was done under the general supervision of Drs. Sutter, Schlorholtz, and Hooton.

FOREWORD

By Amir N. Hanna
Staff Officer
Transportation Research Board

This report presents recommended changes to coal fly ash specifications and test protocols contained in AASHTO Standard Specifications for Transportation Materials and Methods of Sampling and Testing (AASHTO M 295). These changes include modifications to the test methods currently specified for evaluating acceptability of fly ash for use in highway concrete as well as the introduction of new test methods for enhancing such evaluations. The modified specifications and test protocols will guide materials engineers and fly ash producers in evaluating fly ash and assuring that highway concrete is enhanced, and not deleteriously affected, by replacing a portion of the cement in the concrete mixture with fly ash. The information contained in the report will be of immediate interest to state materials engineers and others involved in specifying and evaluating concrete mixtures for use in highway pavements and structures.

Fly ash—a byproduct of coal combustion—is widely used as a cementitious and pozzolanic ingredient in hydraulic cement concrete. The use of coal fly ash in concrete is increasing because it improves some properties of concrete and often results in lower cost of concrete. However, concrete performance is influenced by the chemical and physical compositions of fly ash that are sometimes controlled by regulatory requirements. In addition, current specifications and test methods do not adequately characterize fly ash properties, address the effects of fly ash characteristics on fresh and hardened concrete properties, or consider the alkali content of the cement. Such inadequate characterization may lead to inappropriate use of some materials or unwarranted restrictions on the use of suitable materials.

Previous research has dealt with the effects of fly ash characteristics on concrete properties but not with the applicability of current specifications to the fly ashes that currently are produced. Also, existing test methods for sampling and testing fly ash used in concrete do not adequately address the characterization of fly ash or the performance aspects of highway concrete. Thus research was needed to develop recommendations for improving fly ash specifications and test protocols to help highway agencies better evaluate and use fly ash that will provide acceptable structural performance and durability.

Under NCHRP Project 18-13, “Specifications and Protocols for Acceptance Tests of Fly Ash Used in Highway Concrete,” Michigan Technological University of Houghton, Michigan, worked with the objective of recommending potential improvements to the specifications and test protocols used to determine the acceptability of fly ash for use in highway concrete. To accomplish this objective, the researchers reviewed the practices, specifications, and test methods currently used for evaluating fly ash and investigated their suitability for evaluating fly ash intended for use in highway concrete. The investigation included an extensive laboratory testing program that covered the types and ranges of fly ash currently used or expected to be used in the future in the United States; considered the chemical, physical, and mineralogical characteristics of fly ash; and evaluated the properties of a large number of paste, mortar, and concrete specimens incorporating different types and amounts of fly ash. Based on analysis of test results, changes to AASHTO M 295, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete* (included as Attachment A), that provide guidance on the testing and acceptance of fly ash were recommended. The researchers also proposed new tests for (1) determining the foam index for a coal fly ash and portland cement slurry and (2) determining air-entraining admixture adsorption by coal fly ash (both included in Attachment B). In addition, the researchers proposed changes to ASTM D4607 dealing with the determination of coal fly ash iodine number (also included in Attachment B). Attachment C provides elaborations and detail on several aspects of the research; it is not published herein but is available by searching for *NCHRP Report 749* on the TRB website (www.trb.org).

The recommended new test methods and modifications to existing specifications and test methods would be particularly useful to highway agencies because their use would ensure use of fly ash that will provide the expected performance and durability of highway concrete. Their adoption as part of the AASHTO Standard Specifications for Transportation Materials and Methods of Sampling and Testing is, therefore, suggested.

CONTENTS

Note: Many of the photographs, figures, and tables in this report have been converted from color to grayscale for printing. The electronic version of the report (posted on the Web at www.trb.org) retains the color versions.

SUMMARY

Methods for Evaluating Fly Ash for Use in Highway Concrete

Background

Fly ash—a byproduct of coal combustion—is widely used as a cementitious and pozzolanic ingredient in hydraulic cement concrete. The use of coal fly ash (CFA) in concrete is increasing because it improves some properties of concrete and often results in a lower cost of concrete. However, the chemical and physical compositions of CFA influence constructability, performance, and durability and may contribute to problems, such as cracking and alkali-silica reactivity (ASR) in concrete pavements, bridge decks, and other highway structures. Regulatory requirements have also contributed to changes in CFA properties that may adversely affect concrete performance. In addition, current specifications and test methods do not adequately characterize CFA properties, address the effects of CFA characteristics on fresh and hardened concrete properties, or consider the alkali content of the cement. For example, carbon content of CFA is not usually determined directly but is often assumed to be approximately equal to the loss on ignition (LOI). Such inadequate characterization may lead to unwarranted restrictions on the use of suitable materials. Although a great deal of research has been performed on the effects of CFA characteristics on concrete properties, the research has not dealt with the applicability of current specifications to the fly ashes that currently are produced. In addition, existing test methods for sampling and testing CFA used in concrete do not adequately address the characterization of CFA or the performance aspects of highway concrete. Further research is needed to develop recommendations for improving CFA specifications and test protocols and thus help highway agencies better evaluate and use CFA that will provide acceptable structural performance and durability. NCHRP Project 18-13 was initiated to address this need.

Objective and Scope

The objective of this research was to recommend potential improvements to specifications and test protocols to determine the acceptability of CFA for use in highway concrete. To accomplish this objective, the research included the following:

- A study of existing specifications and classification methods for CFA to recommend changes that would provide better criteria for selection of CFA for a given level of performance.
- An investigation of new test methods for characterizing the strength activity of CFA.
- Identification of new test methods for characterizing the properties of residual carbon in CFA and investigation of approaches for estimating air-entraining admixture or agent (AEA) dosage for CFA.
- Evaluation of the use of CFA to mitigate alkali-silica reaction in concrete and provision of guidance on selection of CFA type and dosage for a specified level of field performance.

Overview of the Project

The research to evaluate new and existing test procedures involved the following five tasks that were performed as separate studies:

- Review of existing specification and testing environment
- Characterization of coal fly ash
- Evaluation of approaches for characterizing strength activity
- Evaluation of test methods for characterizing the effects of carbon on air entrainment
- Evaluation of approaches for assessing ASR mitigation

Existing Specification and Testing Environment

This task was accomplished by reviewing the literature pertaining to CFA tests and specifications. Also, a survey of state highway agencies (SHAs) was conducted to determine the current practices and the needs for new tests and specifications.

Characterization of Coal Fly Ash

Thirty sources of CFA representative of the range of CFA available for use in transportation infrastructure construction in the United States were identified through the survey and industry contacts. A complete characterization was performed for these ashes using a variety of laboratory tests to determine the properties specified in AASHTO M 295-07, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete,* and other properties that should be considered in developing new specifications. The results of this characterization study were compared to certification information obtained from the producers. The task also helped identify areas for improvements in current tests.

Characterization of Strength Activity

Two new approaches for measuring the effect of CFA on the strength of a cementitious mixture were investigated. One approach involved modifications to the current strength activity index (SAI) and the other dealt with a new approach based on the Keil hydraulic index (KHI).

Characterization of the Effects of Carbon on Air Entrainment

This task involved evaluation of the foam drainage test and the foam index test. Additionally, two new tests—the CFA iodine number (based on an existing test ASTM D4607) and the direct adsorption isotherm test (based on ASTM D3860)—were developed and applied to a range of CFAs selected from the 30 identified sources. These four tests were performed on a number of CFAs characterized in terms of the LOI test and selected to provide a broad range in LOI values. The direct adsorption isotherm test was also conducted on various mortar and concrete mixtures to predict the AEA dosage required to achieve a target air content. Hardened air-void analyses were performed to identify differences in the air-void systems resulting from the additional AEA required when CFA was included in the mixtures.

Assessment of ASR Mitigation

This task examined the existing approaches for determining the effectiveness of a CFA at mitigating ASR and evaluated new procedures for assessing this property of CFA. Specifically, this task investigated whether the ASTM C1567 rapid mortar bar test provides better guidance than ASTM C441 and should therefore be included in AASHTO M 295. For this purpose, ASTM C1293 concrete prism tests were conducted to provide a reference. This task also evaluated the alkali leaching test as an alternative approach to the ASTM C441 or ASTM C1567 tests. This study was conducted using eight CFA sources (four Class C ashes and four Class F ashes) selected based on their apparent ability to mitigate ASR, as determined from history and performance.

Results and Conclusions

Results of the literature review and a survey of SHAs suggested the need for improving the tests and specifications for CFA used in highway concrete to better identify those properties affecting concrete performance.

For the fly ash characterization task, 30 fly ash sources were evaluated using the test methods and specification limits stipulated in AASHTO M 295-07. The results of this research suggested a need for refining the existing classification method to include properties known to affect performance, but a completely new approach to classification is not warranted.

The primary distinction between Class F and Class C coal fly ash is the bulk composition based on the sum of silicon dioxide, aluminum oxide, and iron oxide (i.e., $\%SiO_2 + \%Al_2O_3 + \%Fe_2O_3$). However, this classification omits the reporting of calcium. This research has shown a distinct, linear relationship between the sum of the oxides and the calcium content and, therefore, specifying either provides the same result. However, because the calcium content is required for some ASR mitigation practices (e.g., AASHTO PP 65, *Standard Practice for Determining the Reactivity of Concrete Aggregates and Selecting Appropriate Measures for Preventing Deleterious Expansion in New Concrete Construction*), it is recommended that AASHTO M 295 be modified to require reporting the calcium oxide content, expressed as CaO, and also the content of magnesium oxide, sodium oxide, potassium oxide, and the equivalent alkali (Na_2O_e). The CaO and Na_2O_e values are required for determining strategies for ASR mitigation according to AASHTO PP 65.

To address the effect of a CFA on air entrainment, testing was conducted to develop new test methods to predict the AEA demand of any given CFA. These tests included the foam drainage and foam index tests and two new proposed tests: the CFA iodine number and direct adsorption isotherm tests.

After conducting and reviewing a wide range of foam index tests, a modified version of the test method by Harris et al. (2008a) was recommended as a standard test. The modifications included using a range of standard solution concentrations and the solution that achieves a stable foam in a consistent time (i.e., 15 ± 3 min) was chosen for that fly ash. Another modification was the use of a mechanical agitator to minimize operator-induced variability.

Overall, the foam index test was found to be suitable for assessing CFA and AEA interactions but not for measuring the influence of CFA on air entrainment. Even with the proposed improvements, the test has a high level of subjectivity and variability. In spite of its popularity in the concrete industry, the foam index test has not been standardized. Given that use of the test will likely continue, there needs to be a standard approach to conducting the test.

The CFA iodine number and the direct adsorption isotherm tests are recommended to be included in AASHTO M 295 as a Supplementary Optional Chemical Requirement for assessing the adsorption potential of a specific CFA source. From a classification perspective, it is recommended to retain the LOI measure as a means of limiting the maximum carbon content, rather than establishing a maximum CFA iodine number. The CFA iodine number and direct adsorption isotherm test can be used as a means for identifying those CFA sources that have a potential to adversely affect air entrainment. The CFA iodine number test is recommended for use as a screening test. If the test results in a value > 0.1 mg iodine/gram CFA, a direct adsorption isotherm is recommended with a specified AEA, and the capacity determined for the CFA-AEA combination is reported.

Another consideration is the use of powder activated carbon (PAC) for pollution control in power plants, which often increases the adsorption capacity of the CFA without significantly increasing the LOI. Both the CFA iodine number and direct adsorption isotherm tests are extremely sensitive to the inclusion of PAC and they will identify the presence of PAC in the ash and quantify its impact on air entrainment. With the increased use of these pollution control approaches, measurement of the adsorption potential of CFA will increase in importance.

The current available alkali test in AASHTO M 295 takes over 1 month to complete and its precision is questionable. Given that AASHTO PP 65 specifies total alkali limits that exceed the current available alkali limits, it is recommended the available alkali limits from AASHTO M 295 be deleted and requirements for reporting the total alkali contents be inserted as required in AASHTO PP 65.

The current SAI has a minimum strength requirement that can be met by relatively inert materials (e.g., finely ground quartz). Therefore, increasing the 7-day limit from 75% to 85% seems appropriate. However, some Class F fly ashes including those with good long-term strength-gain behavior may fail this requirement. For example, all of the CFAs tested reached acceptable strengths by 90 days of moist curing. Therefore, for determining the strength potential of a CFA, it is recommended the minimum SAI in AASHTO M 295 be raised to 85% at 7, 28, or 56 days of age, with further development focusing on an accelerated pozzolanic activity index-based test.

The current test for ASR mitigation contained in AASHTO M 295 (ASTM C441) uses Pyrex® glass as a synthetic alkali-silica reactive aggregate. For consistency with AASHTO PP 65, ASTM C1567 should be incorporated in AASHTO M 295 with a maximum expansion limit of 0.10% after 14 days of exposure in sodium hydroxide (NaOH) solution.

The research results also indicated that the use of a 28-day expansion limit of 0.10% for evaluation of ASTM C1567 results is not appropriate. In the testing performed, three of the four Class F ashes were not adequate for ASR mitigation when a 28-day expansion limit was used, even at 40% replacement of cement. This performance was not supported by results from the 2-year prism tests conducted according to ASTM C1293.

The ASTM C1293 concrete prism test allows testing both the coarse and fine aggregates, but it is not recommended for inclusion in AASHTO M 295 because it requires an extensive time period to complete (2 years is recommended in ASTM C1293 and AASHTO PP 65).

CHAPTER 1

Introduction

Background

Fly ash—a byproduct of coal combustion—is widely used as a cementitious and pozzolanic ingredient in hydraulic cement concrete. The use of coal fly ash (CFA) in concrete is increasing because it improves some properties of concrete and often results in lower cost of concrete. However, the chemical and physical compositions of CFA influence constructability, performance, and durability and may contribute to problems, such as cracking and alkali-silica reactivity (ASR) in concrete pavements, bridge decks, and other highway structures. Regulatory requirements have also contributed to changes in CFA properties that may adversely affect concrete performance. In addition, current specifications and test methods do not adequately characterize CFA properties, address the effects of CFA characteristics on fresh and hardened concrete properties, or consider the alkali content of the cement. For example, carbon content of CFA is not usually determined directly, but is often assumed to be approximately equal to the loss on ignition (LOI). Such inadequate characterization may lead to unwarranted restrictions on the use of suitable materials. Although a great deal of research has been performed on the effects of CFA characteristics on concrete properties, the research has not dealt with the applicability of current specifications to the fly ashes that currently are produced. In addition, existing test methods for sampling and testing CFA used in concrete do not adequately address the characterization of CFA or the performance aspects of highway concrete. Further research is needed to develop recommendations for improving CFA specifications and test protocols and thus help highway agencies better evaluate and use CFA that will provide acceptable structural performance and durability. NCHRP Project 18-13 was initiated to address this need.

Objective

The objective of this research was to recommend potential improvements to specifications and test protocols to determine the acceptability of fly ash for use in highway concrete.

Research Approach

The research objective was accomplished through a number of activities, including the following:

- A study of existing specifications and classification methods for CFA to recommend changes that would provide better criteria for selection of CFA for a given level of performance
- Identification of new test methods for characterizing the strength activity of CFA
- Development of new test methods for characterizing the properties of residual carbon in CFA and approaches for estimating air-entraining admixture or agent (AEA) dosage for CFA
- Evaluation of the use of CFA to mitigate alkali-silica reaction in concrete and to provide guidance on selection of CFA type and dosage for a specified level of field performance

Report Organization

The report consists of five chapters. Chapter 1 describes the background and research approach. Chapter 2 provides a summary of the literature review pertaining to CFA specifications and test methods and the findings of a survey of state highway agencies. Chapter 3 describes the experimental investigations performed in the project and the process for developing improved methods for characterizing fly ash. Chapter 4 summarizes the results of the investigations. A summary and recommendations for further research are presented in Chapter 5.

The report also includes a list of references and three attachments. Attachment A lists proposed changes to AASHTO M 295, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete.* Attachment B presents a proposed test method for determining the foam index of a CFA and portland cement slurry and proposed changes to test methods dealing with (1) the determination of CFA iodine number and (2) the determination of AEA adsorption by CFA. Attachment C [available by searching for *NCHRP Report 749* on the TRB website (www.trb.org)] provides further details on the research performed in this project.

CHAPTER 2

Literature Review

In 2009, 63 million tons of pulverized coal combustion fly ash, or coal fly ash, was produced in the United States, of which approximately 39% was beneficially utilized (American Coal Ash Assoc., 2011) and the remainder represents an unsustainable solid waste burden to society. The single largest beneficial utilization of CFA is in the production of portland cement concrete (PCC) and concrete products (both as a partial cement replacement and as a constituent in blended cements), which accounts for approximately 50% of the total CFA beneficial use.

CFA has been used in PCC since the 1930s, with the first publication reporting this use appearing in 1937 (Davis et al., 1937). CFA can improve some concrete properties, such as reducing permeability, increasing strength, and mitigating ASR. However, CFA can sometimes result in a reduction in desirable concrete properties, depending upon its physical and chemical nature. Therefore, tests and specifications need to be developed to accurately determine the properties of CFA and help its use to produce concrete with acceptable structural performance and durability.

AASHTO M 295-11, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete,* is the current AASHTO specification for CFA used in concrete. This specification categorizes fly ash produced from coal combustion into two classes—Class F and Class C—and places limits on a number of chemical and physical parameters for both ash classes. The only distinction between the two classes is the requirement for a minimum cumulative weight percentage of the silicon, aluminum, and iron oxides (i.e., sum of the oxides) of 70% for Class F and 50% for Class C. These limits on the "sum of the oxides" generally result in a distinction based on the CFA's pozzolanic and hydraulic reactivity. Class F fly ash is considered to be primarily pozzolanic whereas Class C fly ash, mostly due to the presence of calcium phases, may have cementitious properties in addition to being pozzolanic. In spite of this classification method, Class C ash is generally considered to be a high-calcium-content ash, while Class F is considered to be a low-calcium-content ash (calcium is expressed as percentage of calcium oxide by weight). Existing CFA specifications (e.g., AASHTO M 295 and ASTM C618) have been noted as not being sufficiently specific in classifying CFA (Diamond, 1981) or not being performance oriented (Manz, 1986; Mehta, 1986).

CFA Properties

Coal fly ash is the airborne residue from pulverized coal combustion processes and is typically collected as part of pollution control systems by a variety of means including fabric filters and electrostatic precipitators. These combustion units typically burn pulverized coal as a fuel and, with stable operating conditions and fuel sources, produce CFA with a reasonably consistent quality.

CFA consists primarily of spherical aluminosilicate or calcium aluminosilicate glass particles derived from the mineral matter in both the coal and the extraneous material mined along with coal. The source of the combusted coal is a major factor in determining the composition of the resulting fly ash. Anthracite and bituminous coals are preferred from an energy point of view, but sub-bituminous and lignite (western) coals are increasingly being used because of their abundance, ready access, and lower sulfur content. The principal elemental constituents of CFA are silicon, aluminum, calcium, and iron, all present as oxides (i.e., SiO_2, Al_2O_3, CaO, and Fe_2O_3). Combusting anthracite and bituminous coals will produce fly ash typically containing over 70% by weight SiO_2, Al_2O_3, and Fe_2O_3. Sub-bituminous and lignite coals typically contain a much higher content of calcium-bearing mineral matter and will therefore generally produce a CFA containing significantly higher percentages of CaO (i.e., lime) and a lower cumulative percentage of SiO_2, Al_2O_3, and Fe_2O_3. The lime occurs either as separate crystalline compounds or incorporated into the glass matrix (Hemmings, 1988).

Another important characteristic of CFA is the presence of various forms of carbon intermixed with the inorganic particles, with the carbon occurring typically as discrete particles but also as discrete phases included within inorganic particles. The different forms of carbon may be classified as (1) char particles that are typically 5 to 50 μm or (2) soot and carbon black particles that are typically a micrometer or less in diameter. The char particles can have a wide range of morphologies depending on the coal maceral from which they originated. The texture, porosity, and specific surface area of these chars vary with changes in particle morphology. The general concern with carbon in CFA is the adsorption of organic chemicals onto the carbon, which significantly influences the function of AEAs in concrete mixtures.

Coal Fly Ash in Concrete

CFA has been used in concrete for many years, but it was not until late in the 1940s that its use was widely accepted (Schlorholtz, 2006). Benefits from the use of CFA include improved workability, decreased heat of hydration, reduced concrete cost, potential increased sulfate resistance and ASR mitigation, increased late strength, and decreased shrinkage and permeability (Schlorholtz, 2006). However, use of CFA in concrete can reduce early strengths, reduce AEA effectiveness because of adsorption by carbon in the CFA, and accentuate ASR at some usage levels. Each of these potential problems can be addressed by tests and specifications that accurately predict and specify CFA properties that affect performance of the PCC mixture.

Fly Ash Specifications and Tests

A large portion of the literature pertaining to CFA is focused on concrete performance when CFA is included as a constituent. Most performance concerns are typically associated with the applicable specifications, which are often described as not adequately identifying the characteristics of CFA that affect performance in a concrete mixture. These concerns focus on the chemical and physical classification of the CFA with regard to the inorganic and organic fractions of the ash. In reviewing the literature, it was clear the purpose of existing specifications and tests for CFA are not adequately understood. For example, AASHTO M 295 is not intended to provide a means for predicting performance of a concrete mixture containing CFA but to provide a means of quality control of the CFA proposed for use in the concrete mixture.

CFA specifications have not been adequately revised to reflect the changing practices in the use of CFA in highway concrete. For example, both the air content test and the shrinkage test treat fly ash as fine aggregate, not as a replacement of portland cement as it has often been considered in mixture design. This research performed a critical analysis of these test methods and specification limits to assess their applicability to fly ash commonly used in highway concrete.

Survey of CFA Users and Producers

As part of this research, an on-line survey of state highway agencies (SHAs) was conducted to obtain information on fly ash sources used in pavement concrete and any concerns on existing fly ash specifications. The responses indicated a need for specifications and tests that better predicted performance. Attachment C contains the complete responses to the survey and a summary of its findings.

CHAPTER 3

Methodology

Overview

The research to evaluate new and existing test procedures involved five separate tasks that were performed as separate studies. These tasks are briefly described in this section; details are provided in the following sections of this chapter.

Review of existing specification and testing environment. The literature pertaining to CFA specifications and testing protocols was reviewed to determine the current practices and where improvements may be needed. A survey of SHAs was also conducted to determine the types, characteristics, and ranges of fly ash content currently used in the United States and those likely to be used in the future.

Characterization of coal fly ash. The results of the literature review and SHA survey were used to identify 30 CFA sources for use in this study. The sources were selected to broadly represent the range of CFA currently used in highway construction. The CFA sources selected include Class C and Class F ashes per AASHTO M 295-07 and various beneficiated ashes. (AASHTO M 295-07 was used as the reference for this research; AASHTO M 295-11 was published after this work was completed.)

A characterization protocol was then applied to establish baseline properties of each source. This protocol included all tests currently and commonly used to characterize CFA to provide a means for determining the strengths and weaknesses of these test methods when applied to a wide range of CFA types. It also helped identify other characteristics for use in developing new tests.

Characterization of strength activity. Chemical characterization is based on the bulk chemical composition, which indirectly infers if a fly ash is pozzolanic or has potential for hydraulic reactions in a concrete mixture. The current pozzolanic and strength activity tests were reported as not adequately predicting field performance and in some cases incorrectly identifying inert materials as being reactive (Schlorholtz, 2006). This research evaluated the existing test for pozzolanic activity (i.e., strength activity index), considered potential modifications, and also evaluated a modification of the Keil hydraulic index test (Keil, 1952).

Characterization of the effects of carbon on air entrainment. The residual carbon contained within fly ash can adversely affect air entrainment in concrete as carbon can adsorb the AEA, thereby reducing the effectiveness of the admixture for producing an adequate air-void system (Mehta and Monteiro, 2006). The current LOI test estimates the total residual carbon, but does not determine the adsorption properties of the carbon. In this project, four different tests for measuring the effect of carbon on air entrainment were investigated for inclusion in a new specification. These tests are the foam index test and foam drainage test and modified versions of ASTM test methods: ASTM D4607-94(2006), *Standard Test Method for Determination of Iodine Number of Activated Carbon,* and ASTM D3860-98(2008), *Standard Practice for Determination of Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique,* which are used for characterizing powdered activated carbon (PAC) for water treatment.

Assessing ASR mitigation. AASHTO M 295 does not reference some tests that are currently available to evaluate the effectiveness of a specific CFA for mitigating ASR. Also, there was a need to identify quicker, more effective tests for assessing ASR mitigation. Therefore, existing test methods and a proposed rapid method for determining the effectiveness of a CFA for mitigating ASR in a concrete mixture were evaluated. The existing methods were ASTM C1567, *Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar Bar Method),* and ASTM C1293, *Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction.* The proposed test method was the alkali leaching test (Shehata and Thomas, 2006). Results from the latter test were correlated to those of ASTM C1293 and ASTM C1567.

Also, a number of standard tests were performed on different fly ash sources and the methods used are summarized in this section. Additionally, a number of new tests were developed or evaluated; the process used to refine these tests and their method of application is also summarized. Additional information on the results and procedures is provided in Attachment C.

Materials

CFA Sources

A first step in this research was identification of 30 sources of CFA representative of the broad range of CFA available for use in highway construction in the United States. These sources were identified through a survey of SHAs and contacts within the industry. Material certifications were acquired for CFA sources from over 100 coal combustors located in the United States and compared with a database of CFA properties assembled by the research team. The selected 30 CFA sources consisted of 17 sources of Class F fly ash and 13 sources of Class C fly ash. Details on these sources, producers' certification data, and a property database are provided in Attachment C. The following is a summary of the range of properties of these sources, as obtained from producers' plant certificates:

- Sum of SiO_2, Al_2O_3, and Fe_2O_3: 51.8% to 92.7%
- CaO: 0.9% to 30.6%
- Na_2O_e: 0.3% to 7.9%
- LOI: 0.1% to 5.6%
- Fineness: 10% to 24.0%
- Strength index (7-day test value): 75% to 112%
- Strength index (28-day test value): 80% to 120%
- Water requirement: 93% to 100%
- Density: 2.1 to 2.8 g/cm^3

The properties used as the basis for comparison and selection of the CFA sources included in this study are those commonly collected by producers to meet the requirements of AASHTO M 295-07 specifications. However, other factors were considered such as the geographic distribution, types of coal, combustor, and pollution control measures used at the power plant.

Although producers' certifications were obtained for each identified source, a characterization study was undertaken to confirm the reported CFA properties and to identify CFA sources suitable for use in other portions of this research, and also to evaluate existing specifications and tests. Some of the 30 CFAs were suited for assessing the effects of CFA on air entrainment, evaluating protocols for ASR mitigation, or developing new approaches to measuring CFA strength activity. Based on the characterization study, suitable sources were identified and used where appropriate. The research team obtained additional CFA sources for use in developing the foam index, iodine number, and direct adsorption isotherm tests. Also, for developing these tests, it was necessary to blend ashes to achieve target values of LOI. The CFA sources blended were FA-ZF (LOI = 6.06% wt) and FA-ZE (LOI = 23.3% wt). The blending ratios used were 1:3, 1:1, and 3:1, respectively. A listing of all CFA sources used in the experiments conducted is presented in Table 3.1.

Portland Cement Sources

Three different sources of portland cement designated PC-1, PC-2, and PC-3 were used in the research; the nominal properties provided on mill certifications are summarized in Attachment C. The chemical compositions of these cements were determined using x-ray fluorescence spectroscopy (XRF) and x-ray diffraction (XRD), and other tests were conducted to determine relevant physical properties. Also, for comparison, selected tests were performed using a fourth portland cement source (PC-4); results of these tests are discussed in Attachment C.

Air-Entraining Admixtures

To evaluate new tests for assessing the effects of CFA on air entrainment, it was necessary to select a suite of AEAs that represent the range of AEAs used in highway concrete. The specifications provided by 24 SHAs identified 47 common AEA types. These AEAs were placed in the following five categories identified in *NCHRP Report 578* (Nagi et al., 2007):

- Vinsol resin
- Alpha olefin sulfonate
- Resin/rosin and fatty acid
- Benzene sulfonate
- Combination

Since this classification is based on chemical composition, it was expected that AEAs in the same category would exhibit similar adsorption characteristics. The most commonly used, pre-approved AEA in each category was chosen as the primary AEA in experiments dealing with new tests for evaluating the effects of CFA on air entrainment. The primary AEAs are listed in Table 3.2 as AEA-1 through AEA-5. In later steps, two AEAs were added (i.e., AEA-6 and AEA-9). AEA-6 was included because of its observed low adsorption capacity, and AEA-9 was included in selected tests to verify the results obtained with AEA-5. Other AEAs were included in limited tests for developing the direct adsorption isotherm test.

CFA and Cement Sample Processing

The multiple buckets for each CFA source were combined and homogenized in a rotating drum mixer and a 7 to 9 lb

Table 3.1. CFA sources and tests.

CFA Source				Test						
ID	Class	LOI (% wt)	CaO (% wt)	Strength & ASR Mitigation	Foam Drainage	Foam Index	Iodine Number	Direct Adsorption Measurement	Mortar Verification of Direct Adsorption	Concrete Verification of Direct Adsorption
FA-A	F	0.94	0.82			X	X	X	X	X
FA-G	F	2.32	1.45			X	X	X	X	
FA-H	F	0.25	3.46	X		X	X	X	X	
FA-J	F	1.59	1.28			X	X	X	X	
FA-M	F	0.27	7.17	X						
FA-O	F	1.43	10.2	X		X	X	X	X	X
FA-Q	F	0.38	16.6	X						
FA-T	F	0.45	13.6			X	X	X	X	
FA-U	C	0.54	21.9	X						
FA-X	C	0.42	19.3	X						
FA-ZA	C	0.27	27.3	X						
FA-ZC	C	0.16	30.2	X						
FA-ZE	F	23.30	–		X	X	X	X		
FA-ZF	F	6.06	–		X	X	X	X		
FA-ZG	C	1.22	–		X	X				
FA-ZJ	F	21.34	–				X	X		
FA-ZM	F	10.69	–			X	X	X	X	
FA-ZN	F	3.41	–			X	X	X	X	X
25-75 Blend*	–	10.37	–			X	X	X		
50-50 Blend*	–	14.68	–				X	X		
75-25 Blend*	–	18.99	–				X	X		

*FA-ZF/FA-ZE blends

grab sample was obtained for the characterization study. The remainder was placed in a watertight plastic drum, labeled, and placed in storage. The grab sample was further homogenized by quickly mixing it in a plastic bag and then a 200 g sub-sample was extracted using a sampling tube. The portland cement used in the study was all obtained from the same production lot. The complete process used for obtaining samples of ash for the various tests is discussed in Attachment C.

Table 3.2. AEAs used in assessing the effects of CFA on air entrainment.

AEA ID	Type of Admixture	No. of SHAs with Pre-approval*
AEA-1	Vinsol resin	20
AEA-2	Alpha olefin sulfonate	20
AEA-3	Combination	17
AEA-4	Resin/rosin and fatty acid	23
AEA-5	Benzene sulfonate	10
AEA-6	Resin/rosin and fatty acid	14
AEA-7	Resin/rosin and fatty acid	0
AEA-8	Alpha olefin sulfonate	7
AEA-9	Benzene sulfonate	9
AEA-10	Alpha olefin sulfonate	16
AEA-11	Vinsol resin	19
AEA-12	Resin/rosin and fatty acid	22

* Out of 24 SHAs

Other Materials

Other materials used in this research were Pyrex® glass for ASR testing, calcium hydroxide for the available alkali tests, standard graded and 20-30 graded sand both meeting the requirements of ASTM C778-06, *Standard Specification for Standard Sand,* and various inert fillers used for the strength activity study. These materials were tested prior to use to determine their basic chemical or physical properties and compliance with relevant specifications. All of these materials are covered by standards except the inert fillers. The reported properties of these inert filler materials are summarized in Attachment C.

Characterization of Coal Fly Ash

The following tests were performed on samples of the 30 identified CFA sources. The tests were conducted in accordance with ASTM C311-11a, *Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland Cement Concrete* when applicable. However, some properties were measured using non-standard test methods (e.g., XRD and thermo-gravimetric analysis). The standard tests were generally conducted twice (i.e., tested on different days) to provide an indication of precision. Cement PC-2 was used for the strength and pozzolanic activity indices, autoclave expansion, and air content tests. Specific aspects of the test methods are noted in the following list:

- Moisture content samples were dried overnight at a temperature of 105°C to 110°C.
- LOI samples were ignited to a constant mass at 750°C ± 50°C.
- Oxide samples were analyzed using XRF. The samples were fused using a lithium borate flux to produce a glass disk. Thirteen elements were quantified (Si, Al, Fe, Ca, Mg, Na, K, S, Ti, P, Mn, Sr, and Ba). When expressed as oxides, these elements typically account for over 99% of the bulk composition (expressed on an LOI-free basis) of CFA. Specific samples were also pressed into pellets to better evaluate the sulfur content of the ashes.
- Available alkali (i.e., soluble Na and K, expressed as oxides and sodium oxide equivalent) was determined in accordance with ASTM C311.
- Density was determined using a helium pycnometer.
- Fineness was determined by wet-washing on a 45 µm sieve (#325 mesh).
- Soundness of CFA-cement pastes was determined by the autoclave expansion test. Mixtures containing 20% (by mass of cement) of each CFA were molded at normal consistency.
- Air entrainment determined the amount of AEA-1 required to produce a mortar air content of 18%, in accordance with ASTM C311.
- The strength activity index (SAI) with portland cement was determined using mortar mixtures containing 20% CFA (by mass of cement). The mortars were mixed in nine cube batches; the index values were calculated after 7, 28, and 90 days of standard curing (i.e., limewater cure at 23°C). Control mixtures containing only cement were also mixed on each day. The water requirement for each mortar mixture was determined by maintaining the flow of the mixture within ±5% of the flow of the control mixture. The precision of the test method was evaluated by making seven replicate mixtures containing CFA. In addition, two inert materials (INF-1 and INF-2) were included to check the specification limit for the test method.
- Pozzolanic activity index (PAI) tests were conducted per ASTM C311 on mortar mixtures containing 35% CFA (by volume of cement). The mortars were mixed in six cube batches; the index values were calculated after 7 and 28 days of accelerated curing (i.e., water vapor at 38°C). A control mixture containing only cement was also mixed on each day. The results reflect the average of three tests at 7 and 28 days. The water requirement for each mortar mixture was evaluated by maintaining the flow of the test mixture between 100% and 115%. The precision of the test method was evaluated by making six replicate mixtures containing CFA. In addition, two inert materials (INF-1 and INF-2) were used to check the specification limit for the test method.
- Effectiveness in controlling ASR was determined for each CFA when tested with cement PC-3 in accordance with ASTM C441/C441M-11, *Standard Test Method for the Effectiveness of Pozzolans or Ground Blast Furnace Slag in Preventing Excessive Expansion of Concrete Due to the Alkali-Silica Reaction,* with the modifications described in ASTM C311. Test mixtures contained a 25% replacement (by mass of cement) of CFA for an equivalent amount of portland cement. Control mixtures containing only cement were also mixed on most days to accompany the mixtures containing CFA. At least three repetitions (individual batches mixed on different days) with each control cement (i.e., PC-1, PC-2, and PC-3) were made. In addition, a set of control specimens was made using a very-low-alkali cement that exhibited a nearly negligible expansion (i.e., <0.01% at 56 days) during the Pyrex mortar bar tests. Test results provided the average of tests on three specimens after 14, 28, and 56 days of accelerated curing (i.e., water vapor at 38°C). Selected specimens were monitored until 90 days. INF-2 was also included in the study to evaluate the effect of cement replacement. The precision of the test method was evaluated by testing six replicate mixtures.
- XRD was conducted on samples ground to a fine powder in a micronizing mill. Test specimens were backpacked into a sample holder and then scanned from about 5 to 70 degrees two-theta using a copper x-ray tube and diffracted beam monochromator. Step-size and counting time were selected to produce reasonably smooth diffractograms. Glass content was estimated using the diffuse scattering halo present in the diffractograms.

In addition, quantitative x-ray diffraction (QXRD) and differential thermal analysis/thermal gravimetric analysis (DTA/TGA) tests were conducted on eight CFA samples (H, M, O, Q, U, X, ZA, and ZB) to more accurately describe the properties known to influence reactivity. The QXRD was performed to characterize the crystalline and glass constituents of CFA. Both the relative intensity ratio method (RIR) and the Rietveld method were used to obtain estimates of phase and glass concentrations. The quantitative measurements were repeated multiple times to produce an estimate of the precision of the determinations. The DTA/TGA was performed to provide information on the moisture content and LOI of the bulk CFA, the combustion temperature of the residual coal particles present in the CFA, and the softening temperature of the CFA. In addition, the residue from the thermal analysis test was analyzed using XRD to determine the mineralogy of the devitrified glass.

Characterization of Strength Activity

Two different approaches were investigated to examine tests for measuring the effect of CFA on the strength of a cementitious mixture. One approach considered modifications to the current SAI and another examined an approach based on the Keil hydraulic index (KHI). The CFA sources listed in Table 3.1 were included in this investigation.

Mortar cubes for both the modified SAI and KHI tests were cast following ASTM C109/C109M-11a, *Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens),* except that the water to cementitious materials ratio was kept constant at 0.485 and the sand to cement ratio was 2.75 using graded sand meeting ASTM C778. Cubes were de-molded at 1 day of age and placed in saturated limewater tanks at 23°C as per ASTM C109. Three 2 in. mortar cubes were tested at each age and the strengths were averaged. A compressive testing machine of 100,000 lb capacity specifically fitted for testing mortar cubes was used for all tests.

For the modified SAI tests, all eight CFA sources were tested with each of the three portland cements at 0% wt and 20% wt replacement with CFA. Four Class C ashes were also tested at a replacement level of 35% wt. The specimens with 0% and 20% replacement followed the current SAI test procedure, while the 35% replacement was similar to the PAI test. To evaluate the contribution of an inert filler to strength development, INF-1 was tested at 20% and 35% cement replacement.

Another approach was to modify the KHI previously used for evaluating the reactivity of blast furnace slags (Keil, 1952; Lea, 1970; Hooton and Emery, 1983; Pal et al., 2003). The KHI is expressed by Equation 3.1.

$$Keil\ Hydraulic\ Index = \frac{a-c}{b-c} \times 100 \qquad (3.1)$$

Where:

a = the strength of 70% slag/30% portland cement at time *t*;
b = the strength of 100 percent portland cement at time *t*;
c = the strength of 70% ground quartz/30% portland cement at time *t*

In this test, ground quartz filler with approximately the same fineness as the CFA was included. The difference between this method and other strength activity tests is the KHI test allows for separation of the pozzolanic and hydraulic effects from the physical filler effects. The KHI can range from 0% for an inert material to over 100% if the supplementary cementitious materials (SCM) develop more strength than the portland cement mixture.

To evaluate this method, cement replacements of 20% and 35% (by mass of cement) were used in lieu of the specified 70% replacement for slag. Mortar cubes were tested at ages of 7, 28, and 56 days. The ground quartz specified in the original Keil method was replaced with inert fillers INF-1, INF-2, and INF-3 in an attempt to find an appropriate commercially available filler material for use in the test method.

Using the same type of mortar cube specimens as for the SAI tests, all eight CFAs and INF-1 were tested in a full factorial design with each of the three portland cements (PC-1, PC-2, and PC-3) at 0% and 20% wt replacement of cement with CFA and inert filler. Additionally, four Class C fly ash sources were evaluated at a 35% wt replacement of cement with CFA and inert filler INF-1. Strength tests were conducted at 7, 28, and 56 days of age.

Additional SAI and KHI tests were later conducted using a fourth portland cement source (PC-4) together with all eight CFA sources at 35% wt replacement. For the KHI tests, three inert fillers (INF-1, INF-2, and INF-3) were also tested at 35% wt replacement. These were the only tests conducted with PC-4 and were undertaken to verify results obtained with PC-3. The results of these tests are provided in Attachment C.

Characterization of the Effects of Carbon on Air Entrainment

Foam Drainage Test

The objective of the foam drainage test is to assess interactions between cement, or combinations of cementitious materials, and AEA solutions. The procedure was evaluated to determine if differences in the potential for a CFA to affect air entrainment could be detected. These different procedures are reported in the literature: Gutmann (1988), Cross et al. (2000), and Taylor et al. (2006); differences between these procedures are discussed in Attachment C. The test methods by Cross et al. and Taylor et al. were selected for evaluation. These test procedures were modified by using only CFA as the cementitious material and were evaluated to determine if CFA and AEA interactions could be detected (further discussion of the methodology is provided in Attachment C). The test results indicated that, in most cases, the test does not adequately distinguish the effects of CFAs with significantly different levels of LOI on air entrainment. Because the other tests evaluated in this research showed more promise (e.g., foam index, CFA iodine number, and direct adsorption isotherm tests), the foam drainage test was not further considered in this research.

Foam Index Test

Preliminary Screening of Published Test Methods

Numerous procedures exist for the foam index test (see Attachment C). The foam index test is inherently subjective in determining what constitutes a "stable foam." The various published versions include a range in test variables that must be considered (e.g., mass of CFA and cement in the slurry, AEA solution strength and addition rate, the agitation time, and the overall test time). Another minor yet significant variable is the dimensions of the test container. Because of the extensive number of published tests and the multiple variations of the test, it was decided to evaluate these tests for subjectivity, reproducibility, and ease of use (additional discussion of the test evaluation is presented in Attachment C). The evaluation found the test proposed by Harris et al. (2008a, 2008b, 2008c) presents the best combination of precision, analysis time, and simplicity of approach and was therefore considered for a proposed standard test method. However, a number of modifications were considered.

Standardized Shaking

The process of evaluating the various foam index tests also considered ways of modifying and improving each test with regards to accuracy, reproducibility, or ease of performance. One common concern with all tests was the reproducibility of the agitation process. It was clear that a technician could affect the test results by the vigor with which the agitation (i.e., shaking of the container) was performed. Different technicians could be linked to differences in results. Therefore, it seemed necessary to standardize the agitation process. A very common piece of laboratory apparatus employed was an automated shaker such as the apparatus shown in Figure 3.1. The automated shaker performs similar to a human hand shaking a bottle, ensures repeatable results, and allows a technician to perform multiple tests simultaneously. Because of the bottle type, the Harris procedure lends itself to use of an automated shaker. The time of the shake cycle could be varied to allow the user to select the desired time period.

Standardizing the agitation of the solution should minimize variance due to different agitation methods. To illustrate, four separate Harris procedure foam index tests were performed using FA-ZG (1.22% LOI). Each test consisted of seven foam index determinations. Two sets of tests were performed manually and two used an automated shaker. A summary of the test results is presented in Table 3.3. The use of the automated shaker improved the consistency of the results and greatly reduced the tedium of the test procedure.

Figure 3.1. Harris test using automated shaker.

Another advantage of the automated shaker was the ability to perform multiple tests simultaneously. However, it was determined that, for the operator to have sufficient time to monitor and add AEA to the test specimens during the rest period, a maximum of four concurrent tests could be performed.

Optimum Test Duration

Another variable in the foam index test is the equilibrium state of the CFA and the AEA solution. Some researchers state

Table 3.3. Foam index test results using manual agitation and an automated shaker.

	Shake by Hand		Automated Shaker	
Repetition	Test 1	Test 2	Test 3	Test 4
1	0.12	0.10	0.10	0.11
2	0.14	0.08	0.10	0.13
3	0.10	0.10	0.10	0.11
4	0.12	0.08	0.10	0.13
5	0.10	0.10	0.12	0.14
6	0.10	0.10	0.12	0.13
7	0.10	0.10	0.10	0.13
Average	0.11	0.09	0.11	0.13
Min	0.10	0.08	0.10	0.11
Max	0.14	0.10	0.12	0.14
Standard Dev.	0.02	0.01	0.01	0.01
Coefficient of Variance (%)	14.12	10.35	9.23	9.02

the test is dynamic and is not based on achieving equilibrium (Külaots et al., 2003); other researchers indicate adsorption equilibrium between surfactants such as AEAs and CFA may take hours (Yu et al., 2000); and others note that equilibrium may be achieved in minutes, depending on the carbon characteristics in the CFA (Baltrus and LaCount, 2001). Achieving equilibrium is strongly affected by the combination of materials, the drop-wise addition of AEA solution that causes a constant change in solution concentration, and the inconsistent waiting period for judging the foam stability after addition of AEA solution to the mixture.

Based on the results of numerous foam index tests using different procedures, it was determined that a reasonable time to conduct the test and expect the system to be near equilibrium would be between 10 and 20 min. However, to further support this observation, a series of tests was performed using fly ash FA-ZF (6.06% LOI) and AEA-1 to determine an optimal test duration. The tests were performed following the Harris procedure but the solution concentration was varied to achieve different test durations. For each solution concentration, the test was performed with six replicates (i.e., seven individual determinations of the foam index). The coefficient of variance of the foam index value was used to gauge the reproducibility. This statistic, along with the average test duration for each solution concentration, is presented in Table 3.4. Based on these results, 15 ± 3 min was adopted as the target time for completing a test.

Researchers have noted the need for adjusting solution concentrations depending on the AEA and CFA being tested (Meininger, 1981; Gebler and Klieger, 1983; Dodson, 1990; Freeman et al., 1997; Külaots et al., 1998, 2003, 2004; Separation Technologies, 2000; Zacarias, 2000; Baltrus and LeCount, 2001; Gurupira, 2005; FHWA, 2006; Grace Construction Products, 2006; Harris et al., 2008a, 2008b, 2008c; Stencel et al., 2009). Adjusting the solution concentration to match the adsorption characteristics of the ash improves the test in areas other than reproducibility because using a relatively low concentration solution with a highly adsorbent CFA requires numerous additions of AEA, which increases human error and lengthens the testing time. Also, using relatively higher concentrations leads to shorter testing times, but when only a few drops are needed to achieve an endpoint, a single drop may cause a huge variation in the results.

Standard Solution Concentrations

Identifying standard solution concentrations that satisfy all combinations of fly ash and AEAs would be a desirable provision in a standard foam index test. A numerical analysis was conducted to determine solution strengths using the variables of absolute volume of AEA required to produce a stable foam, initial solution concentration of AEA, and the time to test termination (details are provided in Attachment C). This analysis showed that solution concentrations of 2%, 6%, 10%, and 15% AEA by volume provided a range of test solutions that would allow for completion of the test in 12 to 18 min for most CFA sources.

Recommended Foam Index Test Procedure

For all tests performed using the recommended procedure, a 0.02 mL drop size was used for each AEA incremental addition with solution strengths of 2%, 6%, 10%, and 15% by volume. A procedure is proposed for determining the correct solution strength to complete a foam index test in 15 ± 3 min. This procedure is presented schematically in Figure 3.2.

As shown in Figure 3.2, the technician performs a foam index test with an initial concentration, for example, 6%. If it is determined that the test will require more than 18 min to achieve a stable foam, the technician increases the concentration and restarts the test with a new sample of CFA and cement. Likewise, if the test results in a stable foam in less than 12 min, the technician will decrease the concentration and repeat the test as described. The proposed standard test method is provided in Attachment B.

Foam Index Test Application

Use of the foam index test was demonstrated with AEA-1 through AEA-6 and a series of CFAs ranging in LOI from 0.25 to 22.3% wt. The CFA sources used are summarized in Table 3.1. For these tests, PC-1 was also used.

For the comparison to LOI values, each combination of CFA and AEA was analyzed once with one replicate (i.e., a total of two tests). The results of these tests were averaged to obtain the foam index number for each combination. All foam index

Table 3.4. Mean test times and coefficient of variance (CV%) for foam index tests.

AEA Concentration	12%	8%	4%	3%	2%
Mean Test Time (min)	5.9	10.0	15.0	24.5	31.8
Coefficient of Variance (%)	10.4	7.6	4.6	6.3	7.1

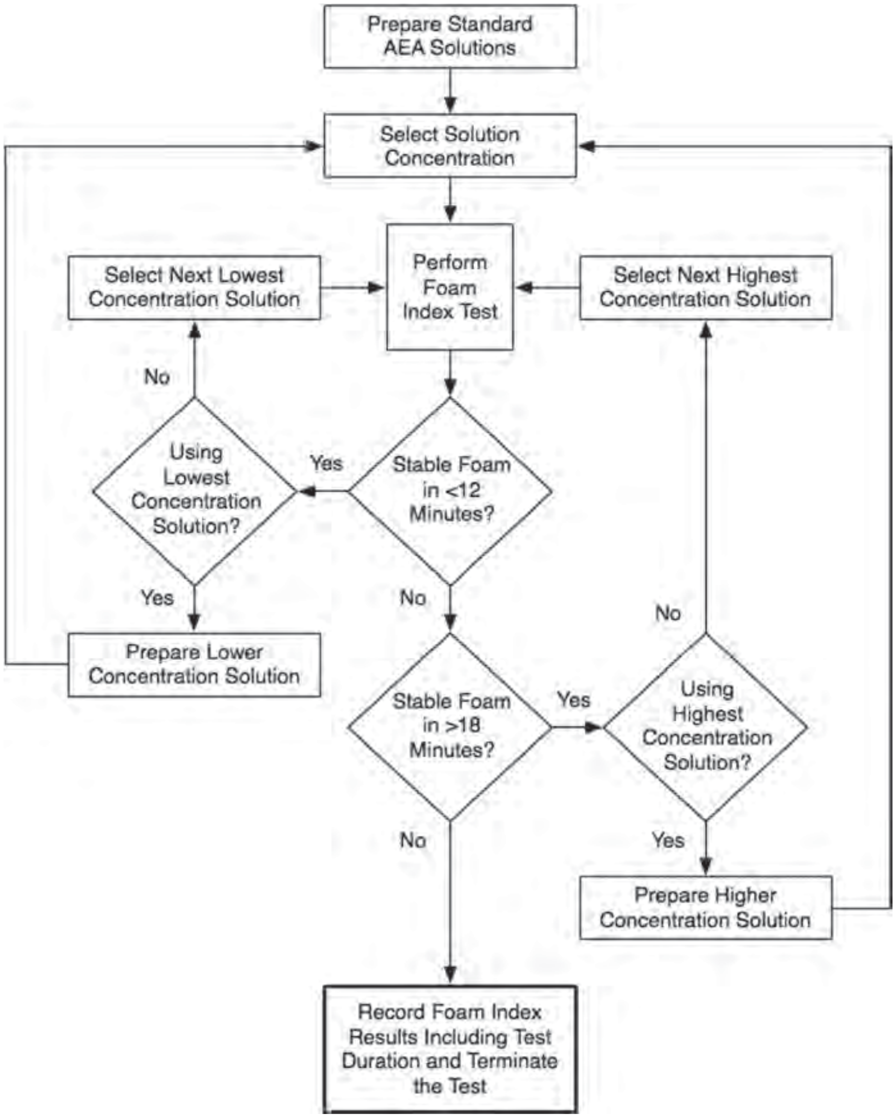

Figure 3.2. Proposed protocol for determining the optimum AEA concentration.

tests reported were performed using the proposed procedure and each test was completed within 12 to 18 min.

In addition, the results of the foam index test were correlated with the results of the CFA iodine number and also the direct adsorption isotherm test. The results of these correlations are presented in Chapter 4.

CFA Iodine Number Test

The iodine number test expresses the adsorption capacity of an activated carbon based on the mass of iodine adsorbed per gram of carbon. Unlike other CFA adsorption capacity indicators such as the foam index test, the CFA iodine number test provides a quantitative measurement for the adsorption capacity of fly ash and can be used directly to characterize and specify CFA for use in portland cement concrete. A significantly modified version of ASTM D4607-94(2006), *Standard Test Method for Determination of Iodine Number of Activated Carbon,* was developed in this project.

ASTM D4607 is intended for use with activated carbon, which is highly adsorbent relative to carbon in CFA. Because of the sulfur content, lime content, and the low adsorption capacity of CFA, this ASTM method should not be used. To address these issues, a new CFA iodine number test was developed that is very different from the current ASTM test although it is based on the same fundamental principle of measuring the adsorption capacity of CFA (i.e., the mass of iodine adsorbed per gram of ash).

The CFA iodine number test is determined from a four-point isotherm. That is, four pre-specified masses of treated CFA are equilibrated with an iodine-water solution and the reduction in iodine liquid-phase concentration is represented as capacity using the Freundlich isotherm equation. The CFA iodine number is defined as the capacity of CFA for iodine at an equilibrium concentration of 0.01 N. Details on developing the test are provided in Attachment C.

Recommended CFA Iodine Number Test Procedure

The recommended CFA iodine number test procedure is provided in Attachment B. A summary of key points is provided below.

CFA Treatment. To treat each CFA, the sample is boiled for 5 min in a solution of 5% wt HCl. The total mass of boiling solution should be at least four times that of the CFA to be treated to ensure the availability of enough HCl to remove all sulfur and acidify the fly ash. The CFA is then filtered using Grade 1 90 mm diameter, cellulose, qualitative filter paper and dried at 103°C to a constant weight.

Mass of Coal Fly Ash Used. In most cases, masses of 80, 40, 20, and 10 g each of CFA were found to be sufficient to produce a suitable and measurable reduction in iodine concentration for CFA with low and medium carbon content. For ash with a high carbon content, 80, 40, or even 20 g may adsorb all the iodine from the solution and result in an unusable isotherm point. In this case, CFA dosages of 10, 5, and 2.5 g or even less can be used.

Iodine Concentration Measurement. The aqueous phase iodine concentration is measured using the procedure presented in *Standard Methods for the Examination of Water and Wastewater* (Method 4500-CI) (Eaton et al., 2005). The solid phase iodine concentration, or CFA capacity, is determined using a mass balance on the isotherm point as described in Equation 3.2.

$$V_o \times C_o = V_f \times C_f + q_{CFA} \times M_{CFA} \quad (3.2)$$

Where:

V_o = initial iodine solution volume, L
C_o = initial iodine solution concentration, mg/L
V_f = final iodine solution volume, L
C_f = final iodine solution concentration, mg/L
q_{CFA} = solid phase iodine concentration (capacity), mg_{iodine}/g_{CFA}
M_{CFA} = mass of fly ash, g

Iodine Number Determination. The four isotherm points are plotted on a log-log scale and a power fit results in the parameters for the Freundlich isotherm equation (Crittenden et al., 2005):

$$q = K \times C^{1/n} \quad (3.3)$$

Where:

q = mass of adsorbate adsorbed per unit mass of adsorbent, mg/g
K = Freundlich isotherm capacity parameter, (mg/g)(L/mg)$^{1/n}$
C = solution concentration, mg/L
$1/n$ = Freundlich isotherm intensity parameter, dimensionless

In the case of the iodine number test, the Freundlich isotherm equation is used to describe the correlation between the iodine solution concentration and the solid phase iodine concentration, or CFA capacity (i.e., mg_{iodine}/g_{CFA}). After determining the Freundlich isotherm parameters, the CFA iodine number can be determined by using 0.01 N (1,270 mg/L) as the iodine aqueous phase concentration in Equation 3.3.

CFA Iodine Number Application

Use of the CFA iodine number test was demonstrated using 14 CFA sources; the results are presented in Chapter 4.

Direct Adsorption Isotherm Test

The fundamental tool for understanding adsorption capacity of organic chemicals onto carbon is the adsorption isotherm. An adsorption isotherm can be used to quantify the adsorption capacity of an adsorbent (i.e., carbon in CFA) and describe the equilibrium relationship between an adsorbent and an adsorbate (i.e., AEA or iodine). The test can be easily performed using conventional laboratory equipment (e.g., flasks, beakers, stir plates). To perform an adsorption isotherm, a mass of adsorbent (i.e., grams of CFA) is mixed with a solution of adsorbate (e.g., milliliters of AEA per liter of solution) for a prescribed period of time sufficient for adsorption to occur. After the prescribed time, the reduction in solution concentration of adsorbate is determined. This process is repeated using a different quantity of adsorbent for additional isotherm data points. An alternative approach is to use the same mass of adsorbent for each isotherm point and vary the solution concentration. The results of the tests for each isotherm data point are plotted on a log-log scale and the data are fit with a power line fit; the slope and intercept of which determine the constants for the Freundlich equation (Equation 3.3) except that q (i.e., capacity) is expressed as milligrams of AEA per gram of CFA.

Once the constants K and 1/n in Equation 3.3 are determined for a given adsorbent and adsorbate, the relationship can be used to determine the amount of adsorbate removed for any adsorbate solution concentration. The test method presented here is based on ASTM D3860-98(2008), *Standard Practice for Determination of Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique,* with modifications made to allow its use with CFA.

Measurement of AEA Solution Concentration

Measuring AEA concentration is problematic since AEAs are mixtures of complex organics. Spectroscopic methods have been used by many researchers to describe the concentration of AEAs. However, the results were always characterized with low accuracy due to the dilution of the sample and the instability of AEA compounds. Several attempts to use total organic carbon measured by the ultraviolet (UV)/chemical (persulfate) oxidation for determining AEA concentration have been unsuccessful. Preliminary tests conducted in this research showed that UV/chemical (persulfate) is a relatively weak oxidant and fails to fully oxidize the complex organic polymers in an AEA mixture.

The chemical oxygen demand (COD) test is often used to measure the dissolved organics in water. The COD test uses extreme oxidation conditions through a strong oxidizing agent [potassium dichromate ($K_2Cr_2O_7$)], strong acid [sulfuric acid (H_2SO_4)], and high temperature (150°C). Nearly all organic compounds are oxidized to CO_2 and measured as milligrams of oxygen consumed per liter of water. To evaluate this approach, serial dilutions of AEA-1, AEA-2, and AEA-5 were made and tested with the commercially available HACH COD kit (TNT821 and TNT822) and DR5000 UV-Vis spectrophotometer. Based on the findings of these tests, this approach was adopted and the terms "AEA concentration" and "COD concentration" are used synonymously.

Quantifying the adsorption behavior of CFA requires an understanding of the behavior of AEA with each component that makes up the concrete system. Mixtures of AEA solutions and gravel, sand, cement, and different CFAs were investigated to determine the effect of each material on the AEA concentration and how AEA partitions in these mixtures. Sorption of AEA onto these materials was divided into *chemisorption* due to the ionic nature of the material and the AEA, and *physical adsorption* due to the presence of adsorptive material such as carbon. Details are provided in Attachment C.

AEA Interaction with Cement

Because cement minerals have an ionic nature, AEAs interact strongly and rapidly with cement. AEA molecules bond to the cement particles via electrochemical bonding (i.e., ionic or covalent), removing the AEA molecules from the solution to the particle surfaces. The sorption process, called "chemisorption," is stronger than physical adsorption and is irreversible under normal conditions.

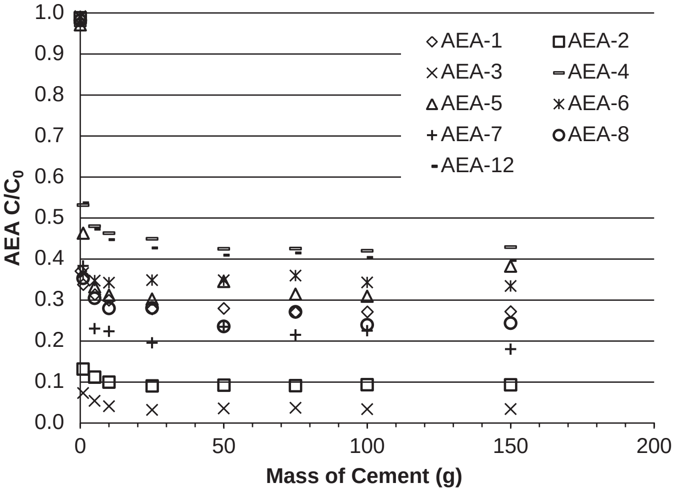

Figure 3.3. AEAs concentration change versus mass of cement.

Figure 3.3 illustrates the *partitioning* of AEA in the case of an AEA solution being equilibrated with various masses of cement. With the addition of only a few grams of cement, the initial AEA solution concentration (C_0) for all AEAs tested decreased to a final solution concentration of less than half of C_0 (i.e., $C/C_o < 0.5$). After adding approximately 10 g of cement, AEA solution concentrations reached a steady level and remained constant regardless of the addition of more cement. This behavior indicates part of the AEA chemisorbs on cement particles early, removing that portion of the AEA from the solution. As the cement content was increased, no more chemisorption occurred even though more active adsorption sites were added (i.e., more cement). The AEA left in the solution is designed by the AEA manufacturers to stay in the solution and participate in stabilizing the air bubbles. The AEA left in the solution after chemisorption is called the "aqueous phase AEA," designated as C. The ratio of the equilibrium aqueous phase AEA concentration to the initial AEA solution concentration is referred to as the "partitioning coefficient," shown as C/C_0 in Figure 3.3.

To use ASTM D3860 with CFA, understanding and correcting for the partitioning of AEA was a necessary modification. Details of these modifications are provided in Attachment C.

AEA Interaction with Aggregate

Equilibration of 0.4% vol. AEA-1 and 0.4% vol. AEA-2 with sand and gravel showed no significant change in the AEA concentrations, suggesting no interaction between AEAs and aggregate. Based on this finding, aggregate was excluded from the isotherm system.

Adsorption Isotherms

The solid phase capacity as well as the initial concentration of the adsorbate governs the amount adsorbed on the solid phase and hence, by difference, the amount of adsorbate remaining in the aqueous phase. The results of the isotherms describe this two-phase equilibrium relationship and can be used to determine the partitioning of the adsorbate between the solid and aqueous phases. For a concrete system, only cement and CFA affect adsorption of AEA. Slag cement was evaluated in this research and performed the same as portland cement with respect to adsorption; results are provided in Attachment C. Two methods of performing adsorption isotherms were evaluated. In one method, cement and CFA isotherms are performed separately and, in the other method, isotherms are performed on a combination of cement and CFA. It was determined that an adsorption isotherm based upon a combination of CFA and cement was required to accurately assess adsorption capacity of CFA. Additional discussion of this approach is provided in Attachment C.

Recommended Procedure for the Direct Adsorption Isotherm Test

Overview. Direct adsorption isotherms are based on equilibrating mixtures of cement, CFA, and AEA solutions to determine the reduction in AEA aqueous phase concentration due to adsorption by the carbon portion of the CFA. Cement is included in the isotherm to quantify the chemisorbable portion of the AEA. An AEA chemisorption isotherm on cement is used as a blank sample to determine the aqueous phase concentration available for adsorption by the CFA. The aqueous phase concentration of the blank is considered to be the initial aqueous phase concentration for determining the CFA isotherm. The reduction in this concentration that results from adding CFA to the system is then used to determine the mass of AEA adsorbed by CFA. CFA capacity is expressed as the ratio of AEA volume adsorbed by CFA to the mass of CFA tested.

The process described above results in one isotherm point. Other isotherm points are obtained by varying the concentration of the AEA solution. Multiple isotherm points can be analyzed using the Freundlich isotherm model that describes the correlation between solid phase (i.e., CFA) capacity and the final AEA aqueous phase concentration. A COD test is used to determine the concentration of AEA in the solution. AEA solutions were prepared on a volume basis.

A recommended test procedure for performing the direct adsorption isotherm test is provided in Attachment B; key points are provided in the following paragraphs.

COD Measurements. COD analyses are performed according to *Standard Methods for the Examination of Water and Wastewater* (Eaton et al., 2005) Method 5220C (closed reflux titrimetric method) or Method 5220D (closed reflux colorimetric method). Use of commercially available kits for performing these tests reduces human error.

AEA Solution Concentrations. Three AEA solution concentrations are used to obtain a three-point isotherm for a constant mass of adsorbent and fly ash. Although any three concentrations in the range of practical interest are appropriate, three AEA aqueous phase concentrations distributed between 300 and 1,300 mg/L COD are preferred for the COD test used. Since most of the AEA mass is chemisorbed into cement particles, it is important to perform a trial blank test that contains 20 g of cement and 200 mL of a known concentration of the AEA solution. The ratio of initial solution COD concentration to the final COD concentration, after equilibration with cement, is used to estimate the three initial concentrations that will be used with cement and CFA to yield equilibrium concentrations between 300 and 1,300 mg/L.

Isotherm Point Setup. To determine all isotherm points, the CFA samples are equilibrated in a 250 mL Erlenmeyer flask at 20°C for 1 h. The AEA solution volume is measured using a 200 mL volumetric flask prior to its addition to the isotherm bottle. A magnetic stirrer is used to keep the contents of the isotherm flask mixed for the entire equilibration time. The solution is filtered using 11 μm filter paper in a vacuum apparatus. The filtrate volume is measured with a 200 mL graduated cylinder.

Chemical Oxygen Demand of Solid Materials. To determine the contribution of the CFA to the total COD of the isotherm point solution, 200 mL of distilled water is added to 80 g of CFA in a 250 mL flask. The solution is stirred using a magnetic stirrer for 60 min then filtered using 11 μm filter paper in a vacuum apparatus. COD measurements of the filtrate provide the concentration of COD released from CFA. The total mass of COD released from CFA in the 200 mL flask can be determined by multiplying the COD concentration by the volume of the solution in the flask. The COD contribution of the cement is compensated for by using 20 g of cement in the blank sample and 20 g of cement in the isotherm data point samples (i.e., the COD contribution of the cement cancels out in this process).

Blanks. A blank sample that contains only cement is required for each initial concentration of AEA utilized. The purpose of the blank sample is to determine the concentration of AEA retained in the solution (i.e., aqueous phase AEA) after chemisorption. Upon introducing CFA to the system, any reduction of this aqueous phase AEA concentration is attributed to the adsorption by the CFA material.

Isotherm Points. For each isotherm point, 40 g of CFA is added to the system. The isotherm point is determined using 20 g of cement, 40 g of fly ash, and 200 mL of AEA solution. Upon adding the solution to the CFA and cement in a 250 mL flask, the mixture is stirred using a magnetic stirrer for 60 min then filtered using 11 μm filter paper in a vacuum apparatus. Then COD measurements for the filtrate are taken.

Mortar and Concrete Mixtures to Evaluate Developed Tests

To evaluate the applicability of the direct adsorption isotherm test for measuring the effects of CFA on air entrainment, a series of mortar and concrete experiments were conducted. For these experiments, control mixtures were prepared using cement only and a dosage of AEA predetermined to achieve a target air content. Test mixtures were prepared with cement, a 25% substitution of CFA (by mass of cement), and admixture dosages intended to achieve air contents similar to those of the controls. The test mixture AEA dosages were determined both by trial and error and by estimating the dosage from the results of the direct adsorption isotherm test using Equation 3.4.

$$\text{AEA Dosage} = (\text{Capacity}_{\text{CFA}} \times \text{WT}_{\text{CFA}}) + \text{AEA Dosage}_{\text{Baseline}} \qquad (3.4)$$

Where:

$\text{Capacity}_{\text{CFA}}$ = AEA capacity from adsorption isotherm, $\text{mL}_{\text{AEA}}/\text{g}_{\text{CFA}}$
WT_{CFA} = weight CFA in mortar mixture, g
$\text{AEA Dosage}_{\text{Baseline}}$ = AEA dosage for cement-only mixture, mL

All mortar mixtures were prepared in accordance with procedures in ASTM C109 and the air content of the mixtures was determined using the procedure described in ASTM C185-08, *Standard Test Method for Air Content of Hydraulic Cement Mortar.* Mortars and concrete were prepared using PC-1 and PC-3 separately. No difference was detected in the performance of the AEAs with either cement; therefore, only the results from PC-1 will be presented.

Control Mortar Mixtures

The control mortar mixtures were prepared with the following:

- Sand – 2,905 g
- Cement – 838.9 g
- Water-cementitious material ratio (*w/cm*) – 0.45
- Paste/aggregate volume ratio – 1.70

The paste/aggregate ratio was determined on an air-free basis. The fine aggregate used was a washed, natural, siliceous glacial sand. Seven AEAs from Table 3.2 were used to make seven separate control mixtures: AEA-1 through AEA-6, and AEA-9. A limited number of mixtures were prepared using AEA-9 to confirm results obtained with AEA-5.

It was impossible to achieve similar air contents in all control mixtures without having very significant differences in the AEA dosage level for each AEA. In some cases, the required AEA dosage would need to exceed the manufacturers recommendations by an order of magnitude. The midpoint of the manufacturer's recommended dosage range was used to prepare the control mixtures and the resulting average air content was used as the target air content for that mixture design. Because the purpose of the mortar tests was to evaluate the applicability of the direct adsorption isotherm test for estimating AEA dosage, it was not necessary to have the same air content in each control mixture.

The plastic air content for each batch of mortar was measured with two replicates and the average of these three measurements was used as the air content for that batch. A total of 17 batches was prepared for each control mixture providing 17 average air content values, the averages of which are presented in Table 3.5 together with the AEA dosages used. For each batch, 4 in. by 2 in. cylinder specimens were prepared, wet-cured for

Table 3.5. Control mortar mixtures AEA dosages for each air entrainer.

Air Entrainer	Manufacturer Recommended (oz/cwt)	Control Mixture Dosage (oz/cwt)	Resulting Average Target Air Content (% vol.)
AEA-1	0.2–4	2.1	8.9
AEA-2	0.12–1.5	0.8	5.3
AEA-3	0.2–1	0.6	5.6
AEA-4	0.5–3	1.8	7.2
AEA-5	0.5–1	1.8*	6.7
AEA-6	0.2–3	1.5	6.6

* AEA-5 required twice the manufacturer's maximum recommended dosage to achieve the minimum air content. Further discussion is provided in Chapter 4.

28 days, and then processed for hardened air determination using a modified version of ASTM C457/C457M-11, *Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete.* The measurements were performed using a flatbed scanner (Sutter, 2007).

Mixtures with Coal Fly Ash

Table 3.1 lists the sources of CFA used in preparing the mortar test mixtures. Although the CFA was substituted for cement on a weight basis, it was important to ensure the total paste volume for the control mixtures and the CFA mixtures remained the same. Therefore, the total weight of cementitious material and water added for the CFA mortar mixtures was less than used in the control mixtures because of the lower specific gravity of the fly ash relative to portland cement. However, the CFA remained at 25% of the portland cement by mass and the *w/cm* remained at 0.45. Table 3.6 presents the total cement, fly ash, and water used in the CFA mortar test mixtures, and the specific gravity of each ash.

To determine the AEA required to achieve the target air content for the CFA test mixtures, a trial-and-error approach was used. First, the CFA mixture was prepared using the control mixture dosage. Then, six additional batches were prepared with an incremental change in the AEA dosage for each batch, resulting in mortars with air contents above and below the target air content. The measured air content was considered to match that of the control mixture air content if it was within ± 0.5% vol. air. Once a test mixture with the target air content was established, that mixture design was repeated to validate the mixture proportions. For each batch, 4 in. by 8 in. cylinder specimens were made, wet-cured for 28 days, and later used for hardened air determination.

A second set of mortar test specimens with 25% replacement of cement with CFA was prepared with an AEA dosage estimated using the direct adsorption isotherm method. In this method, the AEA adsorbed by the mass of CFA was calculated, and the AEA dosage of the control mixture was increased by this amount.

Table 3.6. Mixture design for the CFA mortar test mixtures.

ID	Cement (g)	CFA (g)	Sand (g)	Water (g)	CFA Specific Gravity
FA-H	597.4	199.1	2,905	379.9	2.08
FA-T	612.1	204.0	2,905	388.7	2.48
FA-A	605.6	201.9	2,905	384.9	2.19
FA-O	609.8	203.3	2,905	387.4	2.41
FA-J	612.7	204.2	2,905	389.1	2.50
FA-G	606.4	202.1	2,905	385.3	2.31
FA-ZN	606.7	202.2	2,905	385.5	2.32
FA-ZM	606.7	202.2	2,905	385.5	2.32

Control Concrete Mixtures

The control concrete mixtures were prepared with the following:

- Cement – 564 lb/yd^3
- *w/cm* – 0.44
- Coarse/fine aggregate weight ratio – 60/40
- Aggregate/Paste volume ratio – 2.1

The fine aggregate was washed, natural, siliceous glacial sand meeting the specifications of ASTM C33/C33M-11a, *Standard Specification for Concrete Aggregates.* The coarse aggregate was a crushed siliceous glacial gravel meeting the requirements of ASTM C33 #67 grading.

AEA-1, AEA-2, and AEA-6 (from Table 3.2) were used to make three separate control mixtures with dosages of 1.9, 1.7, and 2.1 oz/cwt cement, respectively. The dosages were established by trial and error to attain a total air content of 6.5% ± 1.5%. Air contents of the fresh concrete were determined using ASTM C231/C231M-10, *Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method.*

Mixtures with Coal Fly Ash

A 25% by weight substitution of CFA for cement (i.e., 141 lb/yd^3) was used. The paste to aggregate ratio was held constant when the CFA was introduced to the mixture by adjusting the volume of aggregate used in each mixture. All mixtures were prepared in duplicate. Three CFA sources were evaluated (see Table 3.1).

Two sets of concrete test mixtures with CFA were prepared. One set was used to show how the mortar mixture designs with CFA relate to the concrete mixture designs with CFA. For these test mixtures, the AEA dosage used was based on the results for mortars that used the same combination of AEA and CFA. For example, if a mortar mixture with a particular CFA-AEA combination required a 50% increase in AEA dosage, then the AEA dosage for the concrete mixtures of the same combination was increased by 50%. The second set of mixtures was used to evaluate the efficacy of the direct adsorption isotherm test for predicting AEA dosages in concrete. In this method, the AEA adsorbed by the mass of CFA in the concrete mixtures was calculated, and the AEA dosage of the control mixture was increased by this amount.

Air Determination for Mortars

To determine air-void system parameters, slabs were cut from samples of hardened mortar, ground, and lapped. Lapped slabs from 11 of the mortars were analyzed following ASTM C457 Method B to establish data for calibration of the automated method. These 11 slabs were then inked with black marker to render the solid constituents black. A white powder (ground wollastonite) was packed into the voids, and the prepared slabs were scanned on a flatbed scanner (Sutter, 2007). The scanned images were analyzed using a system based on ASTM C457 Method B to develop calibration constants for use in the remainder of the analyses.

Slabs from mortars prepared with FA-G, FA-H, and FA-J were polished, treated, and scanned. The mortars having air contents approximating that of the control mortars were analyzed. Slabs from the hardened control mortars were also prepared, scanned, and analyzed. All six AEAs were evaluated for each of the mortars in a total of 36 individual analyses (i.e., 18 control mortars and 18 mortars containing fly ash).

Assessment of ASR Mitigation

The purpose of this study was to evaluate different approaches for determining the effectiveness of a CFA for mitigating ASR and to evaluate new procedures for assessing this important property of CFA used in portland cement concrete. Currently AASHTO M 295 stipulates mortar bar expansion limits based on ASTM C441 (as modified in ASTM C311). In the ASTM C441 procedure (also known as the Pyrex mortar bar test), mortar bars are made with high-alkali cement (0.95% to 1.05% Na_2O_e) and different replacement levels of CFA and stored at 38°C, and the percentage reduction in expansion due to the pozzolan or slag is calculated. AASHTO M 295 requires the expansion of the CFA mixture to be not greater than that of a control mixture containing low-alkali cement. However, laboratory programs typically test a fixed 20% by mass CFA replacement to rank CFA sources in terms of their relative ability to reduce expansion, not to determine a required level of fly ash. A better approach, which is allowed in ASTM C311, would be to test a CFA at different cement replacement levels to determine the minimum attainable level of expansion.

To investigate if the ASTM C1567-11 rapid mortar bar test provides better guidance than ASTM C441, tests were conducted on concrete prisms according to ASTM C1293-08b, to provide a reference. Also, use of the alkali leaching test as an alternative approach to either the ASTM C441 or ASTM C1567 tests was investigated.

Procedure for Evaluating ASTM C1567 and C1293

The specimens for ASTM C1567 and ASTM C1293 tests were made using cement PC-3 because it meets the requirements of both tests. The alkali-silica reactive aggregate used was crushed gravel from Sudbury, Ontario, containing reactive argillites and greywacke. The eight CFA sources listed in Table 3.1 were used (and also used in the strength activity tests).

Concrete Prism Tests. For the ASTM C1293 tests, 707 lb/yd^3 of cementitious material that combines PC-3 with CFA replacement levels of 0%, 20%, 30%, and 40% was used. Reagent NaOH was added to the mix water to obtain an alkali equivalence of 1.25% by mass of cement and the alkali loading of the concrete of 8.8 lb/yd^3 for the 100% cement control mixture. Although the mill certification noted the Na_2O_e to be 0.86%, it was later determined to be 1.06%, causing an overdose of alkalis in all the concrete mixtures (i.e., the control actually had 10.3 lb/yd^3 of Na_2O_e). This higher alkali content will result in higher expansions than should be obtained from the standard ASTM C1293 test.

The levels of CFA replacement used were selected to cover the range required by the AASHTO PP 65-11, *Standard Practice for Determining the Reactivity of Concrete Aggregates and Selecting Appropriate Measures for Preventing Deleterious Expansion in New Concrete Construction.* According to this practice, the Sudbury aggregate would be considered as moderately reactive (R1). Therefore, the required CFA replacement levels required for ASR mitigation of pavements exposed to de-icer salts (i.e., Level 4 and Class S3) would be prevention level Y. For CFA with CaO contents of less than 18% and alkali contents of less than 3%, the required level of cement replacement would be 25%. For CFA with alkali contents of up to 4.5%, the required level of cement replacement would be 30%. Calcium and alkali levels for the eight fly ashes are shown in Table 3.7. According to Table 6 of AASHTO PP 65, the required cement replacements would be 30% for FA-M and 25% for FA-H, FA-O, and FA-Q. However, because the other four Class C fly ashes have CaO contents greater than 18%, this table cannot be used.

Concrete mixtures were prepared and consolidated into molds with the aid of a vibrating table. Three prisms were

Table 3.7. Cement replacement levels based on AASHTO PP 65.

	CFA Source							
	FA-H	FA-M	FA-O	FA-Q	FA-U	FA-X	FA-ZA	FA-ZC
CaO (%)	3.46	7.17	10.2	16.6	21.9	19.3	27.3	30.2
Na_2O_e (%)	2.27	4.23	2.04	1.63	2.15	6.85	3.97	2.50
min. % Fly Ash	25	30	25	25	X	X	X	X

Note: An X indicates that Table 6 of AASHTO PP 65 cannot be used.

cast with studs for length change measurements, and a fourth prism was cast for potential petrographic analysis. After casting, the molds were covered with wet burlap and plastic to reduce surface drying. The prisms were de-molded after 24 h, initial length measurements were taken, and then sealed inside 5 gal plastic pails above water with moist filter paper around the sides (per ASTM C1293). The prisms were never soaked in water to avoid leaching alkalis from the hardened concrete. However, this does mean that some of the early length change can be from moisture absorption and not ASR-related expansion. For this reason, the 7-day reading rather than the initial 1-day reading was used as the datum reference reading.

At 1 day of age, the pails containing the concrete prisms were placed in a curing room controlled at 38°C, removed from the curing room the day prior to measurements and cooled to 23°C, and returned to the curing room after length change measurements were completed. Length changes were measured at the intervals required in ASTM C1293 and averaged for the three prisms.

Accelerated Mortar Bar Tests. Accelerated mortar bar tests were conducted in accordance with ASTM C1567. All eight CFA sources were tested using a full factorial design with portland cement PC-3 replacement at 0%, 20%, 30%, and 40% wt. In addition, FA-H was tested at 10% and FA-X and FA-ZA were tested at 50% wt replacement.

The mortar bars (1 in. by 1 in. by 11.25 in.) were cast for each mixture. For the first 24 h after mixing, the molds were placed in sealed containers above water to maintain a humid environment. The bars were then de-molded and immersed in water, in sealed containers, and placed in an oven at 80°C. Initial length measurements were made at 2 days in accordance with ASTM C1567. The bars were then immersed in NaOH solutions preheated to 80°C, and length change was measured at 14 and 28 days, and other intermediate ages.

Alkali Leaching Tests. The alkali leaching test (Shehata and Thomas, 2006) was evaluated as a possible test for determining if a cement-CFA combination is effective in mitigating ASR. In this test, cement paste samples are ground to a powder and then immersed in 0.25 mol/L OH^- solution using equal concentrations of NaOH and KOH. The solutions are measured for Na^+, K^+ and OH^- after 7 and 28 days of leaching. The change in concentration of the solution is calculated to determine the quantities bound to or released from the cement paste. Details of the alkali leaching test are provided in Attachment C.

CHAPTER 4

Findings

CFA Characterization Study

Results obtained from characterization tests of the 30 sources of CFA are summarized in this section. Additional results are provided in Attachment C.

Chemical Tests

The bulk chemical properties of the CFA samples are summarized in Tables 4.1 through 4.3. The bulk chemical (XRF) test results for CFA are reported on an oven-dry basis in an oxide format. A comparison of reported and measured values is provided in Attachment C.

Table 4.1 lists the major elements, moisture content, and LOI test results. The minor oxides and available alkali test results (i.e., lime-soluble alkali content at 28 days per ASTM C311) are given in Tables 4.2 and 4.3, respectively. In Table 4.3, aNa_2O and aK_2O denote the available sodium and potassium values determined by flame photometry, respectively. The available alkali content is expressed as equivalent sodium oxide ($\%Na_2O_e = \%Na_2O + 0.658 \times \%K_2O$). The available alkali test results are reported on an as-received basis (no drying prior to the test).

The bulk chemistry values for minor components and available alkali results for the 30 samples of CFA showed a good range of composition (see Tables 4.2 and 4.3). Seven Class C ashes and three Class F ashes failed the AASHTO M 295 requirement for available alkali not to exceed 1.50% wt. However, two of the Class C ashes failed the requirement by a very small margin (1.58% wt for sample FA-ZD and 1.52% wt for sample FA-W). The available alkali test exhibits rather poor precision, and it is therefore unlikely these two CFAs were significantly above the specification limit. However, the total alkali data, primarily sodium oxide content, indicated an increase in alkali content for the CFAs that failed the available alkali test as seen in Figure 4.1. Class F fly ashes containing potassium as the major alkali (below 1% on the graph) tend to exhibit little correlation between total and available alkali. In contrast, when sodium becomes the primary alkali, as is the case for most Class C ashes, there is a good correlation between total alkali and available alkali. This could be used to simplify the process of determining if a particular source of CFA meets the alkali requirements. The available alkali test takes about 35 days to complete. Total alkali could easily be determined on a daily basis and could be used to provide a quick determination of the alkali content of CFA.

Another investigation was conducted to evaluate the amount of sodium and potassium that could be extracted from CFA when it was mixed with water (i.e., water-soluble alkali). This investigation included the eight CFA samples that had been selected for extensive ASR testing; the test results are summarized in Table 4.4.

The water-soluble alkali test utilized a sample of 1.75 g of the as-received CFA mixed with 200 mL of water and stirred for 1 h. The suspension was filtered using a medium-texture filter paper; solids were then washed using room temperature water. The effect of the number of wash cycles on the measured soluble alkali content was small for three, six, and nine wash cycles (±0.02% soluble alkali expressed as $\%Na_2O_e$). The test results obtained using three washes are given in Table 4.4.

The results presented in Tables 4.3 and 4.4 indicate soluble alkali of about an order of magnitude lower than the available alkali, when expressed as $\%Na_2O_e$, except for two Class C fly ashes (FA-X and FA-ZA). Coal fly ash FA-ZA was obtained from a power plant that reportedly adds trona to the raw coal feed to enhance the performance of its electrostatic precipitators and that appears to influence the amount of soluble sodium in the CFA.

Table 4.1. Summary of CFA chemical properties.

ID	Class	Sum of Oxides (% wt)	Moisture (% wt)	LOI (% wt)	SiO_2 (% wt)	Al_2O_3 (% wt)	Fe_2O_3 (% wt)	CaO (% wt)
FA-A	F	92.52	0.04	0.94	61.6	27.9	3.02	0.82
FA-B	C	67.62	0.14	1.19	39.2	20.3	8.12	14.3
FA-C	F	88.99	0.10	1.22	59.8	22.2	6.99	2.24
FA-E	F	87.76	0.01	1.84	55.5	24.6	7.66	2.78
FA-F	F	90.62	0.04	2.26	56.9	27.3	6.42	1.09
FA-G	F	89.89	0.02	2.32	53.9	27.7	8.29	1.45
FA-H	F	91.26	0.02	0.25	60.9	25.7	4.66	3.46
FA-I	F	89.45	0.09	2.19	62.4	20.1	6.95	1.81
FA-J	F	91.90	0.09	1.59	46.0	23.6	22.3	1.28
FA-K	F	83.50	0.08	1.61	46.9	23.2	13.4	6.85
FA-L	F	84.80	0.05	0.94	47.2	19.3	18.3	6.79
FA-M	F	81.85	0.07	0.27	60.3	16.6	4.95	7.17
FA-N	F	86.90	0.03	0.80	46.6	19.9	20.4	5.33
FA-O	F	79.81	0.03	1.43	58.9	16.2	4.71	10.2
FA-P	F	73.34	0.05	0.13	50.2	16.9	6.24	14.0
FA-Q	F	74.34	0.07	0.38	50.3	19.2	4.84	16.6
FA-R	F	73.27	0.02	0.07	50.7	15.3	7.27	15.3
FA-S	F	70.55	0.02	1.01	43.2	20.4	6.95	17.1
FA-T	F	77.41	0.11	0.45	44.8	23.1	9.51	13.6
FA-U	C	65.80	0.02	0.54	39.4	19.4	7.00	21.9
FA-V	C	63.00	0.06	0.50	38.0	19.3	5.70	24.8
FA-W	C	62.83	0.03	0.33	35.7	20.0	7.13	24.2
FA-X	C	61.63	0.06	0.42	36.7	19.5	5.43	19.3
FA-Y	C	62.77	0.03	0.20	37.1	19.5	6.17	24.4
FA-Z	C	61.21	0.04	0.17	34.4	20.0	6.81	26.5
FA-ZA	C	55.32	0.02	0.27	32.8	16.8	5.72	27.3
FA-ZB	C	61.66	0.05	0.16	37.2	19.3	5.16	25.7
FA-ZC	C	53.09	0.02	0.16	31.4	15.9	5.79	30.2
FA-ZD	C	54.27	0.02	0.20	30.8	17.6	5.87	29.2
FA-ZL	C	61.52	0.05	0.32	36.3	19.4	5.82	18.0

Table 4.2. Summary of CFA minor elements.

					Total Alkali		
ID	MgO (% wt)	SO_3 (% wt)	Na_2O (% wt)	K_2O (% wt)	Na_2O_e (% wt)	P_2O_5 (% wt)	TiO_2 (% wt)
FA-A	0.84	0.19	0.30	2.80	2.14	0.18	1.45
FA-B	3.53	3.22	5.84	1.10	6.56	0.56	1.24
FA-C	1.79	0.65	0.92	2.27	2.41	0.19	1.00
FA-E	1.23	0.70	1.02	2.09	2.40	0.23	1.20
FA-F	0.83	0.31	0.24	2.43	1.84	0.37	1.58
FA-G	1.15	0.24	0.38	2.88	2.28	0.37	1.36
FA-H	1.12	0.18	1.46	1.23	2.27	0.07	1.09
FA-I	1.33	0.33	0.89	1.93	2.16	0.17	0.95
FA-J	0.99	0.97	0.43	2.73	2.23	0.18	1.08
FA-K	1.79	1.27	0.83	1.68	1.94	0.66	1.16
FA-L	0.80	2.27	0.58	2.15	1.99	0.18	0.99
FA-M	2.58	1.07	3.34	1.36	4.23	0.30	0.87
FA-N	1.12	1.15	0.62	3.03	2.61	0.43	0.95
FA-O	3.13	0.86	1.19	1.29	2.04	0.46	0.85
FA-P	4.38	0.90	3.32	1.71	4.45	0.35	0.99
FA-Q	3.46	0.88	1.05	0.88	1.63	0.25	1.28
FA-R	5.24	0.83	1.51	2.23	2.98	0.13	0.59
FA-S	3.41	2.01	2.53	0.76	3.03	0.74	1.32
FA-T	2.97	0.96	1.00	1.44	1.95	0.74	1.50
FA-U	4.84	1.07	1.54	0.92	2.15	1.05	1.43
FA-V	4.64	1.41	1.62	0.50	1.95	1.03	1.55
FA-W	4.79	2.30	1.80	0.53	2.15	1.16	1.54
FA-X	5.21	2.56	6.33	0.79	6.85	0.56	1.32
FA-Y	5.45	1.24	1.65	0.52	1.99	1.22	1.48
FA-Z	4.78	1.93	1.70	0.39	1.96	1.33	1.64
FA-ZA	6.41	3.56	3.70	0.41	3.97	0.94	1.28
FA-ZB	4.84	1.71	1.13	0.44	1.42	1.70	1.45
FA-ZC	7.93	2.64	2.32	0.27	2.50	0.93	1.32
FA-ZD	7.64	3.25	2.19	0.30	2.39	0.86	1.33
FA-ZL	4.44	3.43	7.45	0.86	8.02	0.60	1.29

Table 4.3. Summary of CFA minor elements and available alkali results.

ID	Mn_2O_3 (% wt)	SrO (%wt)	BaO (%wt)	aNa_2O (%wt)	aK_2O (%wt)	AA (%wt)
FA-A	0.01	0.07	0.10	0.12	0.74	0.61
FA-B	0.04	0.54	1.15	4.21	0.65	4.64
FA-C	0.06	0.05	0.10	0.31	0.70	0.77
FA-E	0.04	0.10	0.16	0.45	0.73	0.93
FA-F	0.02	0.11	0.12	0.10	0.66	0.54
FA-G	0.03	0.12	0.14	0.13	0.77	0.64
FA-H	0.02	0.10	0.18	0.48	0.32	0.69
FA-I	0.06	0.08	0.19	0.35	0.70	0.81
FA-J	0.03	0.04	0.07	0.18	0.89	0.77
FA-K	0.03	0.15	0.23	0.28	0.44	0.56
FA-L	0.04	0.05	0.05	0.25	0.77	0.76
FA-M	0.05	0.20	0.56	1.61	0.58	1.99
FA-N	0.05	0.05	0.19	0.21	0.85	0.76
FA-O	0.02	0.12	0.16	0.46	0.42	0.73
FA-P	0.08	0.31	0.63	1.59	0.68	2.04
FA-Q	0.13	0.31	0.38	0.57	0.36	0.81
FA-R	0.07	0.29	0.55	0.42	0.54	0.77
FA-S	0.03	0.35	0.70	1.53	0.37	1.77
FA-T	0.03	0.29	0.47	0.50	0.59	0.89
FA-U	0.04	0.34	0.70	1.02	0.52	1.37
FA-V	0.06	0.39	0.77	1.20	0.35	1.43
FA-W	0.03	0.37	0.78	1.28	0.36	1.52
FA-X	0.04	0.69	1.57	4.57	0.42	4.88
FA-Y	0.02	0.37	0.81	1.14	0.31	1.34
FA-Z	0.04	0.44	0.84	1.23	0.27	1.41
FA-ZA	0.03	0.47	0.83	2.16	0.22	2.31
FA-ZB	0.02	0.44	0.97	0.73	0.26	0.90
FA-ZC	0.02	0.54	0.90	1.62	0.18	1.74
FA-ZD	0.03	0.55	0.95	1.46	0.18	1.58
FA-ZL	0.05	0.67	1.51	5.67	0.54	6.03

AA = available alkali

Table 4.4. Water-soluble alkali for selected samples of coal fly ash after three wash cycles.

ID	Na_2O (% wt)	K_2O (% wt)	$\%Na_2O_e$ (% wt)
FA-H	0.07	< 0.01	0.07
FA-M	0.19	0.02	0.20
FA-O	0.06	0.01	0.06
FA-Q	0.06	0.01	0.07
FA-U	0.06	0.01	0.07
FA-X	1.05	0.08	1.10
FA-ZA	0.72	0.01	0.73
FA-ZC	0.18	0.01	0.19

Physical Tests

The results of the physical tests conducted in accordance with ASTM C311 are presented in this section. The values for physical properties are the average of two tests conducted on different days. The values for SAI, PAI, and ASR tests were typically obtained from a single test. However, tests on six or seven of the mortar mixtures were repeated to provide an estimate of the precision of the test results. Information on the precision of the various tests is provided in Attachment C.

The soundness (i.e., autoclave expansion) values for the various CFA sources ranged from –0.03% to 0.12%, which is substantially lower than the specification limit given in AASHTO M 295 of 0.8% expansion. A good correlation was noted between expansion and bulk %MgO as shown in Figure 4.2.

The mass retained on a #325 mesh sieve as determined from the fineness tests ranged from 10% to 27%. Class C fly ashes tended to have lower fineness values than Class F fly ashes as shown in Figure 4.3. All of the samples easily met the 34% maximum fineness limit.

Particle size distributions for the thirty sources of CFA, PC-1, INF-1, INF-2, two additional CFA sources (FA-ZM and FA-ZN), and a commercially available ground blast furnace slag used in strength modeling experiments were determined by scanning electron microscopy (SEM) and quantitative image analysis. The results are summarized in Attachment C together with a description of the methodology used.

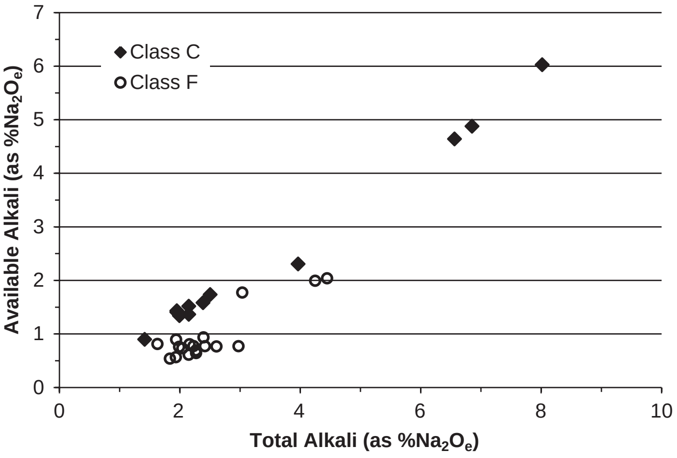

Figure 4.1. Total alkali versus available alkali.

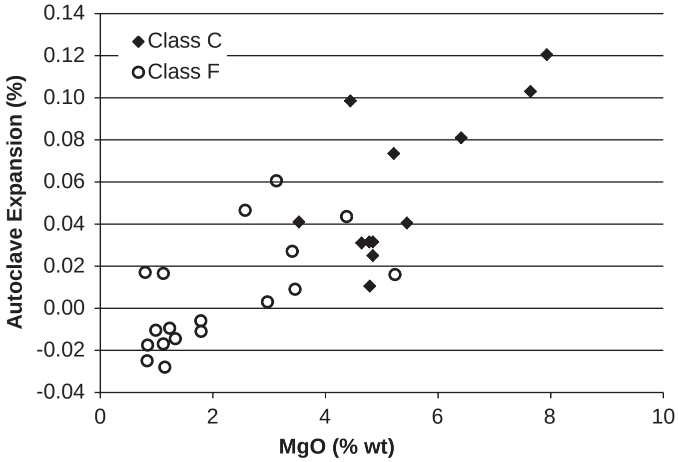

Figure 4.2. Percentage of magnesium oxide versus autoclave expansion.

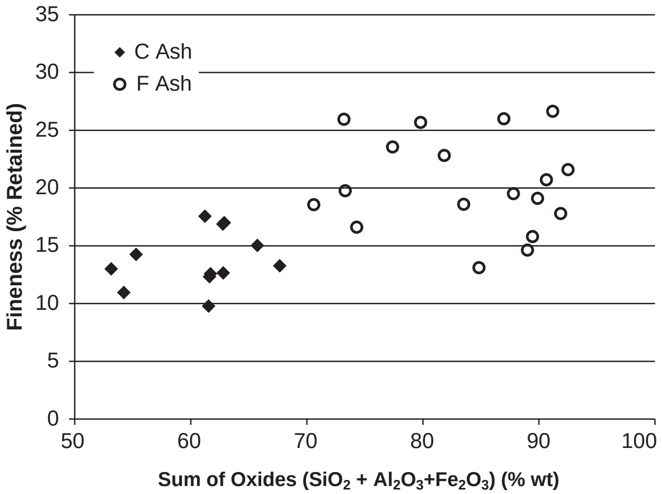

Figure 4.3. Sum of the oxides versus fineness.

Table 4.5. Physical properties of the CFA samples.

ID	Fineness (% retained)	Density (g/cm^3)	Soundness (% expansion)	AEA dosage (oz/cwt)
FA-A	20.6	2.19	−0.02	1.88
FA-B	13.2	2.56	0.04	1.59
FA-C	20.7	2.35	−0.01	1.72
FA-E	19.5	2.36	−0.01	1.62
FA-F	20.7	2.25	−0.02	1.99
FA-G	19.1	2.31	−0.03	1.98
FA-H	26.6	2.11	−0.02	1.70
FA-I	15.8	2.43	−0.01	2.10
FA-J	17.8	2.50	−0.01	2.01
FA-K	18.6	2.53	−0.01	2.01
FA-L	13.1	2.55	0.02	1.62
FA-M	22.8	2.41	0.05	1.39
FA-N	26.0	2.49	0.01	1.34
FA-O	25.7	2.41	0.06	2.63
FA-P	19.8	2.58	0.04	1.21
FA-Q	16.6	2.47	0.01	2.18
FA-R	25.9	2.45	0.02	1.24
FA-S	18.6	2.53	0.03	2.16
FA-T	23.6	2.48	0.00	1.24
FA-U	15.0	2.61	0.02	1.59
FA-V	17.0	2.68	0.03	2.15
FA-W	12.6	2.71	0.01	1.60
FA-X	12.3	2.66	0.07	1.24
FA-Y	16.9	2.62	0.04	1.20
FA-Z	17.6	2.70	0.03	1.12
FA-ZA	14.2	2.73	0.08	1.22
FA-ZB	12.6	2.61	0.03	1.20
FA-ZC	13.0	2.77	0.12	1.20
FA-ZD	10.9	2.71	0.10	1.34
FA-ZL	9.8	2.57	0.10	1.37

Density of the 30 CFA sources ranged from about 2.1 to 2.8 g/cm^3. Class C fly ashes tended to have higher densities than Class F fly ashes. Because density is a uniformity measure of CFA sources, only a variability metric is specified (i.e., ±5% relative to a moving average). Since only single samples were obtained from the various sources, the uniformity of each product stream could not be evaluated. This test method utilized a helium pycnometer for the determinations, which provided good repeatability [within lab (single-operator) standard deviation at about 0.005 g/cm^3, suggesting a maximum difference between duplicate determinations (d2s) of about 0.015 g/cm^3]. Therefore, use of a helium pycnometer appears appropriate for evaluating product uniformity.

Mortar Air Content Tests

The results of the mortar air content tests conducted in accordance with ASTM C311 using PC-2 and 20-30 sand are also summarized in Table 4.5. At least four mortar mixtures were made for each CFA sample. The first mortar consisted of CFA, cement, sand, and water (i.e., no AEA was added). Subsequent mortar mixtures were made with increasing amounts of AEA. The target air content for the second and third mortar mixtures were 15% to 18% and 18% to 21%, respectively. The test results were then used to estimate by interpolation the amount of AEA needed to produce a mortar containing 18% air; additional mortar mixture was made on a different day to verify this value. All of the final mortar mixtures had air contents of 18 ± 1%.

The dosage of AEA required to produce 18% mortar air content ranged from about 1.1 to 2.7 oz/cwt of cementitious material, which is within the "normal" dosage recommended by the manufacturer. Class C ashes, except FA-V, tended to require less AEA than Class F ashes to produce 18% mortar air. In addition, AEA dosage did not appear to correlate well with LOI or fineness as shown in Figure 4.4. Similar to density, AEA dosage is also a uniformity measure for CFA sources and, therefore, only a variability metric is specified. This test method needs to be updated to reflect the current practice of substituting CFA for an equal mass of cement rather than as a replacement of fine aggregate. This updated test method would effectively change the aggregate to cement ratio from 3.0 to 4.0. Additional testing would indicate if the change would impact the AEA dosage for the various CFAs.

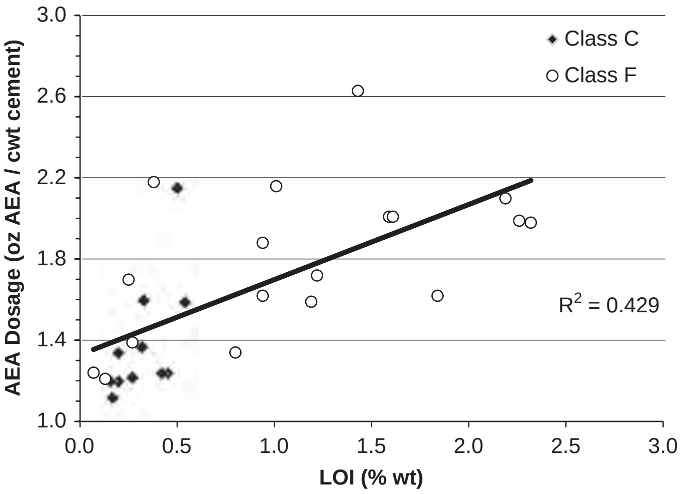

Figure 4.4. LOI versus AEA dosage.

Table 4.6. SAI test results.

ID	Compressive Strength Ratio (% control) 7-day SAI	28-day SAI	91-day SAI	Water Required (% control)
FA-A	85	91	107	100.6
FA-B*	95	99	108	96.4
FA-C	86	90	110	99.4
FA-E	82	89	104	99.2
FA-F	83	84	98	98.9
FA-G	83	90	103	98.9
FA-H*	79	83	107	98.2
FA-I	81	91	107	98.9
FA-J	81	86	98	98.3
FA-K	79	89	99	96.4
FA-L	77	87	96	98.3
FA-M	78	91	105	98.3
FA-N	79	83	96	99.2
FA-O	79	85	100	98.3
FA-P	85	90	107	96.9
FA-Q	87	96	111	96.9
FA-R*	84	87	102	96.1
FA-S	88	93	99	96.9
FA-T	82	86	95	96.9
FA-U	88	106	102	96.9
FA-V	93	100	107	96.9
FA-W	95	110	108	96.9
FA-X*	99	97	95	96.1
FA-Y	91	100	105	96.4
FA-Z	90	103	108	96.9
FA-ZA	92	93	100	96.9
FA-ZB*	96	101	112	96.2
FA-ZC*	97	100	103	95.8
FA-ZD*	95	98	103	96.1
FA-ZL	104	99	104	95.3

* Denotes the average of two batches

SAI Tests

The results of the standard SAI test are given in Table 4.6. The test specimens consist of mortar cubes that are broken in unconfined compression after curing for specific periods of time. The test results are expressed in terms of a compressive strength ratio (expressed as a percentage) to the portland cement-only control mixture, which was prepared at a fixed water-cement ratio (0.485).

The SAI tests are formulated on a mass basis. Coal fly ash is used to replace 20% of the cement in the mixture and water (expressed as a percentage of the control mixture water) is added as required to produce a flow within ±5% of the control mortar. The test results showed that all CFA mixtures met both the 7- and 28-day specification limits (i.e., 75% minimum). Test results also showed reasonable trends with respect to CFA classification (i.e., the sum of silicon, aluminum, and iron oxides) that indicated Class F ashes had a lower rate of strength gain at early ages (see Figure 4.5). However, after extended moist curing (e.g., 90 days), the trend is no longer evident. None of the mixtures approached the maximum water requirement limit of 105%.

SAI tests were also conducted on mixtures made with ground quartz to determine if finely ground materials without pozzolanic properties meet the specification requirements. Tests conducted using ground quartz materials INF-1 and INF-2 produced 7- and 28-day test results of 81% and 74%, respectively, for INF-1, and 74% and 73%, respectively, for INF-2. These values are very close to the specification limit. Further discussion of this issue is provided later in this chapter.

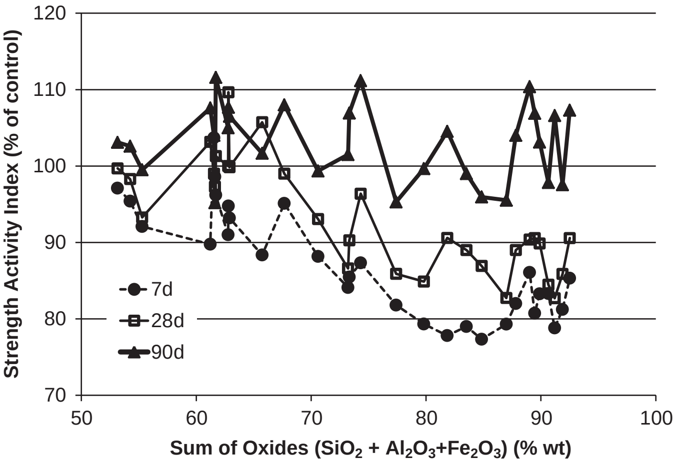

Figure 4.5. Strength activity index versus sum of the oxides.

PAI Tests

Like the SAI tests, the PAI tests use mortar specimens, but the mixture formulation and curing regime differ between the two tests. The PAI tests were formulated on a volume basis. Coal fly ash replaced 35% of the volume of cement in the mixture and water is added to produce a flow within 100% to 115%. Cubes were cured at 38°C ± 2°C in sealed containers (i.e., wide-mouth mason jars). The PAI test is slightly accelerated in comparison to the SAI test; results are given in Table 4.7.

The PAI test results showed reasonable trends with respect to CFA classification (i.e., the sum of silica, alumina and iron oxide) that indicated Class F ashes had a lower rate of strength gain at early ages (see Figure 4.6). However, after 28 days of moist curing at 38°C, the trend was no longer evident. All CFA mixtures met the 28-day specification limit of at least 75% of the control strength. However, some Class C ashes showed little or no strength gain from 7 to 28 days as shown in Figure 4.7, which is somewhat different than the SAI test results. PAI tests were also conducted using INF-1 and INF-2. The 7- and 28-day test results using INF-1 were 57% and 58%, respectively, and 51% and 56%, respectively, for INF-2. Therefore, this test method was able to discriminate between ground quartz and CFA samples. None of the mixtures approached the maximum water requirement limit of 105%.

ASR Mortar Bar Tests

The results of the ASR mortar bar tests conducted in accordance with ASTM C311 are summarized in Table 4.8.

Table 4.7. PAI test results.

ID	Compressive Strength Ratio (% control) 7-day PAI	Compressive Strength Ratio (% control) 28-day PAI	Water Required (% control)
FA-A	64	93	99.8
FA-B	94	95	96.5
FA-C*	72	102	99.0
FA-E	70	92	99.0
FA-F	64	91	100.6
FA-G	67	95	99.0
FA-H	66	91	102.3
FA-I	80	99	97.7
FA-J	67	88	97.3
FA-K	68	90	95.7
FA-L	77	92	96.9
FA-M	76	98	99.0
FA-N*	62	91	99.0
FA-O	69	88	99.8
FA-P	80	103	94.4
FA-Q	83	109	94.4
FA-R	78	94	92.4
FA-S	82	98	95.7
FA-T	72	92	95.7
FA-U*	86	105	95.7
FA-V	96	103	93.6
FA-W*	112	112	93.6
FA-X*	95	87	93.6
FA-Y	88	99	93.6
FA-Z	91	89	93.2
FA-ZA	90	85	93.2
FA-ZB	94	100	94.0
FA-ZC*	86	80	91.5
FA-ZD	84	86	92.8
FA-ZL	87	84	92.8

* Denotes the average of two batches

The values listed in Table 4.9 were calculated using the raw data in Table 4.8. Because these were calculated, the test results in Table 4.8 were reported to an extra significant figure (i.e., three decimal places rather than the normal two commonly used for this type of test result). The values in Table 4.9 are reported as integers as that is roughly the precision of the base measurements. The values in Table 4.9 are the measured expansions relative to the low-alkali control cement PC-1, low-alkali lab cement PC-2, and high-alkali control cement PC-3. This particular table will be used to illustrate an anom-

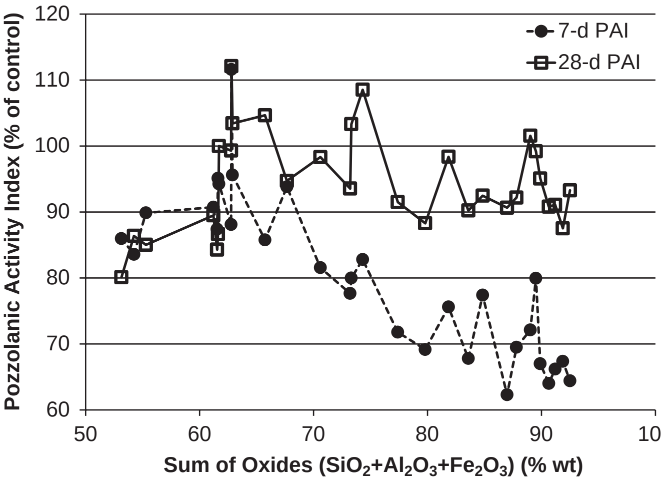

Figure 4.6. Sum of the oxides versus pozzolanic activity index.

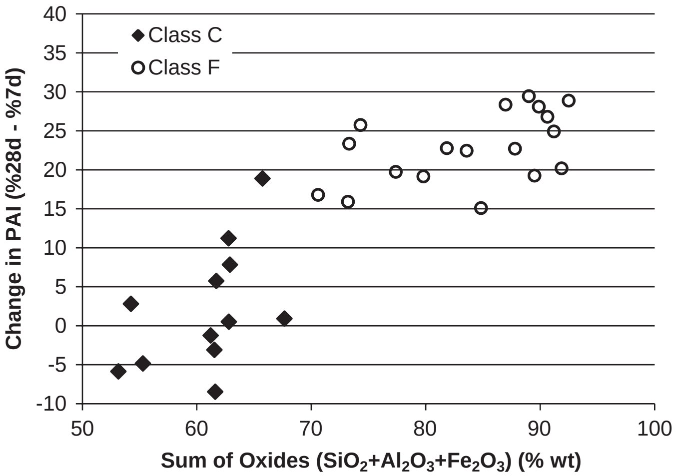

Figure 4.7. Sum of the oxides versus change in pozzolanic activity index from 7 to 28 days of curing.

Table 4.8. Expansion measured in ASR tests.

ID	Expansion (%) 14 days	Expansion (%) 28 days	Expansion (%) 56 days	Difference (56 – 14 days)
PC-1 only	0.202	0.262	0.285	0.083
PC-2 only	0.306	0.331	–	–
PC-3 only	0.488	0.579	0.610	0.122
FA-A	0.147	0.152	0.152	0.005
FA-B	0.193	0.234	0.262	0.069
FA-C*	0.174	0.185	0.188	0.015
FA-E	0.184	0.190	0.191	0.007
FA-F	0.192	0.200	0.200	0.008
FA-G	0.183	0.193	0.196	0.013
FA-H	0.179	0.187	0.188	0.009
FA-I*	0.158	0.167	0.170	0.014
FA-J	0.197	0.208	0.209	0.012
FA-K	0.179	0.195	0.199	0.020
FA-L	0.224	0.246	0.253	0.029
FA-M	0.192	0.221	0.238	0.046
FA-N	0.190	0.203	0.205	0.015
FA-O	0.199	0.216	0.220	0.021
FA-P*	0.227	0.254	0.270	0.054
FA-Q	0.159	0.166	0.170	0.011
FA-R	0.193	0.209	0.216	0.023
FA-S	0.214	0.239	0.252	0.038
FA-T	0.189	0.201	0.202	0.013
FA-U*	0.284	0.312	0.325	0.045
FA-V	0.285	0.305	0.314	0.029
FA-W*	0.253	0.278	0.287	0.026
FA-X	0.220	0.259	0.282	0.062
FA-Y	0.283	0.305	0.312	0.029
FA-Z	0.286	0.306	0.316	0.030
FA-ZA	0.275	0.302	0.319	0.044
FA-ZB	0.276	0.304	0.316	0.040
FA-ZC*	0.350	0.380	0.400	0.040
FA-ZD	0.372	0.394	0.409	0.037
FA-ZL	0.205	0.273	0.313	0.108

* Denotes the average of two batches

Table 4.9. ASR test results expressed as relative expansion.

	Relative Expansion (% control mixture)					Reduction in Expansion (% control mixture)		
	PC-1 control cement Na_2O_{eq} = 0.51%			PC-2 lab cement Na_2O_{eq} = 0.53%		PC-3 control cement Na_2O_{eq} = 1.04%		
ID	14 days	28 days	56 days	14 days	28 days	14 days	28 days	56 days
FA-A	73	58	53	48	46	70	74	75
FA-B	96	89	92	63	71	60	60	57
FA-C	86	70	66	57	56	64	68	69
FA-E	91	73	67	60	57	62	67	69
FA-F	95	76	70	63	60	61	65	67
FA-G	91	74	69	60	58	63	67	68
FA-H	89	71	66	58	56	63	68	69
FA-I	78	64	59	51	50	68	71	72
FA-J	98	79	73	64	63	60	64	66
FA-K	89	74	70	58	59	63	66	67
FA-L	111	94	89	73	74	54	58	59
FA-M	95	84	84	63	67	61	62	61
FA-N	94	77	72	62	61	61	65	66
FA-O	99	82	77	65	65	59	63	64
FA-P	112	97	95	74	77	54	56	56
FA-Q	79	63	60	52	50	67	71	72
FA-R	96	80	76	63	63	60	64	65
FA-S	106	91	88	70	72	56	59	59
FA-T	94	77	71	62	61	61	65	67
FA-U	141	119	114	93	94	42	46	47
FA-V	141	116	110	93	92	42	47	49
FA-W	125	106	101	83	84	48	52	53
FA-X	109	99	99	72	78	55	55	54
FA-Y	140	116	109	92	92	42	47	49
FA-Z	142	117	111	93	92	41	47	48
FA-ZA	136	115	112	90	91	44	48	48
FA-ZB	137	116	111	90	92	43	47	48
FA-ZC	173	145	140	114	115	28	34	35
FA-ZD	184	150	144	122	119	24	32	33
FA-ZL	101	104	110	67	82	58	53	49

aly in the current testing scheme, although the test method has positive aspects.

Results from the ASR mortar bar tests, Table 4.9, are illustrated in Figures 4.8 and 4.9 for Class C and Class F fly ashes. The 14-day expansion relative to the expansion of the low-alkali control cement is plotted on the *x*-axis and the 14-day reduction in expansion relative to the high-alkali cement is plotted on the *y*-axis. There is no specification limit for the percentage of reduction in expansion for CFA for the Pyrex glass-mortar bar test method but earlier versions of AASHTO M 295 used an absolute maximum expansion limit of 0.020%, except for

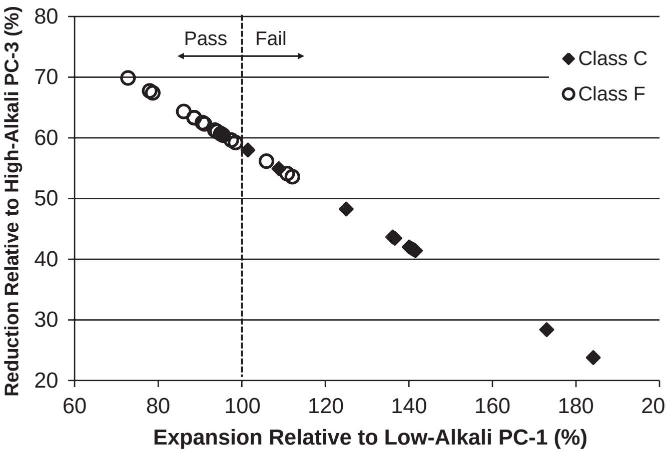

Figure 4.8. Expansion relative to PC-1.

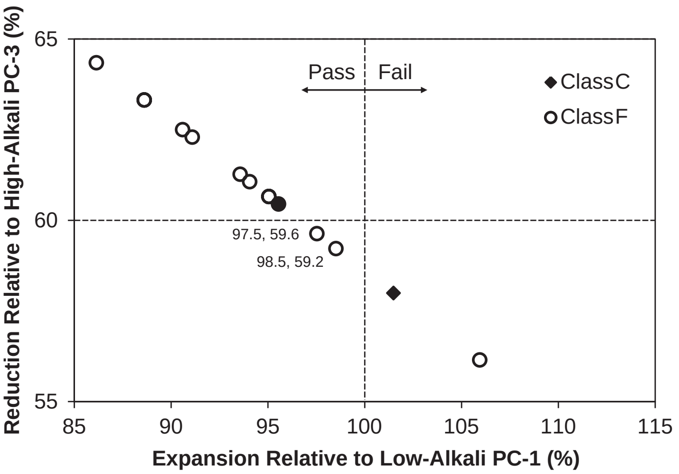

Figure 4.9. Expansion relative to PC-1 near failure/ acceptance limit.

natural pozzolans for which a minimum reduction in expansion of 75% was the acceptance criterion. The current limit of 100% expansion relative to the low-alkali cement and the proposed 60% reduction in expansion limit relative to the high-alkali cement are in general agreement as they tend to rank the 30 CFA sources used in this project in a similar order. Class C ashes are generally on the lower right-hand side of Figure 4.8 and Class F ashes are generally on the upper left-hand side. Only two Class F CFAs failed the 60% reduction criterion while passing the current specification limit of 100% maximum, low-alkali control (see Figure 4.9). Therefore, the two failure limits are in reasonable agreement, especially if the precision of the test method is considered.

To further analyze the results with consideration of the alkali content of the cement, test results using PC-2 as the low-alkali control cement are also presented in Table 4.9 and Figure 4.10. These results show that only two CFAs (both Class C) failed the specification limit given in AASHTO M 295, which is substantially different from the results obtained when cement PC-1 was used in the experiments.

Considering the various performance criteria for expansion at 14 days, the results are summarized as follows:

- Fourteen of thirty CFAs (three Class F and eleven Class C) failed the current specification limit of 100% (relative to low-alkali cement PC-1).
- Two Class C fly ashes (FA-ZC and FA-ZD) failed the current specification limit of 100% (relative to low-alkali cement PC-2).
- None of the CFAs (either Class F or Class C) passed the old specification limit of 0.020% (absolute expansion) at a replacement level of 25%.
- Fifteen of the CFAs (four Class F and eleven Class C fly ashes) would fail the assumed criteria of 60% reduction in expansion criterion (relative to high-alkali cement PC-3).

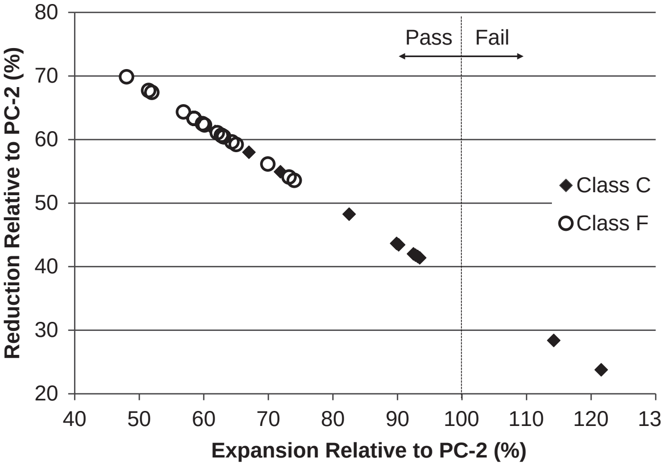

Figure 4.10. Expansion relative to PC-2.

Clearly, the apparent performance of a CFA changes depending on the cement used in the test because of the inherent variability in cement chemistry as illustrated in Figure 4.11 (Roy, 2002). The figure illustrates that a 0.02% limit cannot be obtained with cement alkali contents greater than 0.4% expressed as Na_2O_e. In addition, low-alkali cements (Na_2O < 0.6%) tend to exhibit expansions ranging from 0% to 0.2% at 14 days. Therefore, the current specification limit differs depending on cement selection. All 30 CFA samples reduced the expansion to below that obtained using ground quartz and, therefore, they appear to have potential for reducing ASR expansion.

X-ray Diffraction, Thermal Analysis, and CFA Mineralogy

Material characterization was performed using qualitative and quantitative x-ray diffraction, and thermal analysis methods to establish the mineralogy of the CFA sources. The results are presented in Attachment C.

Summary of Precision Estimates for the Methods

The precision of each test method was evaluated using a procedure described by Youden et al. (1951) and Taylor (1990). This method utilizes the difference between duplicate tests to estimate the pooled standard deviation of the analytical method; the results are presented in Attachment C.

Discussion of Characterization Test Results

The bulk chemistry values presented in this chapter indicated the CFA samples exhibited a wide range of composition and physical properties. Eighteen of the CFAs were designated as Class F and twelve were designated as Class C

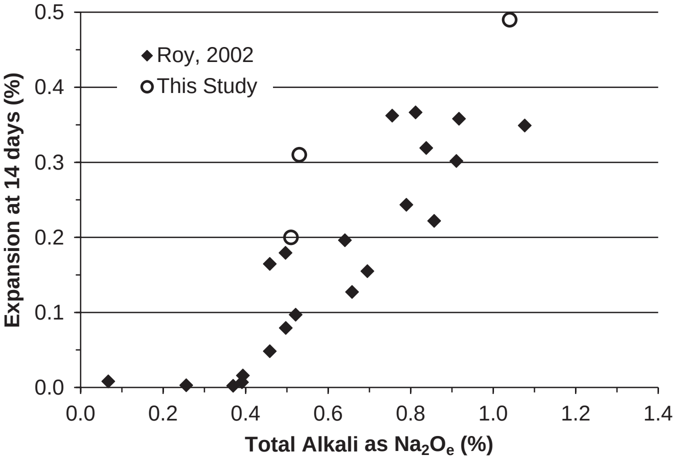

Figure 4.11. Expansion in the Pyrex mortar bar test.

Table 4.10. Test results for mandatory AASHTO M 295 requirements.

Test	Spec. Limit	Fly Ashes Not Meeting Requirements	
		Class F	Class C
$SiO_2 + Al_2O_3 + Fe_2O_3$	Only defines class		
SO_3	5.0% max.	None	None
Moisture Content	3.0% max.	None	None
Loss on Ignition	5.0% max.	None	None
Fineness	34% max.	None	None
Strength Index	75% min.	None	None
Water Requirement	105% max.	None	None
Soundness	0.8% max.	None	None

ash. In addition, the CFAs exhibited a good range of physical properties. All of the CFA samples met the mandatory chemical requirements given in AASHTO M 295 (see Table 4.10); the majority of the CFAs met the mandatory physical requirements; and some of the CFAs failed the optional requirements (see Table 4.11). The majority of the failures pertained to alkali content or the effectiveness of controlling ASR. Some of the test requirements (e.g., the multiple factor) are not supported by the test results in Table 4.12). For example, the maximum LOI and fineness values observed during this study did not approach the specification limits. The requirements for a maximum fineness of 34% and a maximum LOI limit of 5% constrain the multiple factor to a maximum value of 170, which is substantially lower than the specification limit of 255 (the multiple factor is no longer part of AASHTO M 295).

Current class limits for CFA are based on the sum of oxides (i.e., silicon, aluminum, and iron oxides). However, some researchers suggest this approach has shortcomings in two general areas related to performance: the classification does not include calcium oxide and is based on bulk chemistry, not crystalline and glass phase content (Diamond, 1981; Manz, 1986; Mehta, 1986; Bumrongjaroen et al., 2011). The data in Table 4.12 for the 30 ash sources used in this study are sorted by the sum of oxides. Also, the results for CaO and CaO + MgO content are presumed as examples of other compositional parameters that could be used to classify CFA. However, these variables are related to each other, as shown in Figures 4.12 and 4.13.

As shown in Figure 4.12, there is a clear linear relationship between the sum of oxides and CaO content and using either produces the same results as a criterion for classifying the CFAs. The addition of MgO as shown in Figure 4.13 incrementally improves the linear regression (based on the R^2 value) as a result of adding an additional analyte to the regression analysis but does not change the classification of the ashes. The three Class C ashes falling slightly below the regression line (FA-B, FA-X, and FA-ZL) show the same trend as the other CFAs but are biased low because elements present in significant concentrations are not included in the regression. For the 30 ashes analyzed, adding BaO and Na_2O into the sum of oxides, and plotting against CaO, results in an R^2 value of 0.99 with no change in CFA classification.

The ultimate goal of a classification method is to group CFAs that have similar physical and chemical properties without excessive testing, and then to measure and report other properties that are known to affect performance within a specific class. The existing AASHTO M 295 classification system is adequate at grouping similar materials but needs refinement with respect to reporting other properties. For example, particle characterization based on crystalline composition (Bumrongjaroen et al., 2011) provides a rigorous analysis of the fly ash microstructure, but the inherent variability within a given source makes characterization at the particle level impractical. Classification based on bulk properties (e.g., composition, fineness) has worked for many years, and correlations between bulk properties and performance have been developed by highway agencies. It is recommended to establish distinct limits for Class F and Class C ashes based on the sum of the oxides and to report the CaO content and the total alkali content.

Table 4.11. Test results for optional AASHTO M 295 requirements.

Test	Spec. Limit	Fly Ashes Not Meeting Requirements	
		Class F	Class C
Available Alkali	1.5% max.	M, P, S	B, W, X, ZA, ZC, ZD, ZL
Multiple Factor	255% max.	None	Not applicable
Drying Shrinkage	0.03% max.	Not tested	Not tested
Uniformity of Air-Entraining Dosage	20% max.	Not tested	Not tested
Effectiveness in Controlling ASR	100% max.	L, P, S	All failed except B
Sulfate Resistance	0.05% for high resistance	Not tested	Not tested

Table 4.12. Summary of CFA properties (calculated from test results).

ID	Sum of Oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$)	Class	CaO (% wt)	CaO + MgO (% wt)	Multiple Factor
FA-ZC	53.2	C	30.2	38.1	2.1
FA-ZD	54.2	C	29.2	36.9	2.2
FA-ZA	55.3	C	27.3	33.7	3.8
FA-Z	61.2	C	26.5	31.2	3.0
FA-ZL	61.5	C	18.0	22.5	3.1
FA-X	61.6	C	19.3	24.5	5.2
FA-ZB	61.7	C	25.7	30.5	2.0
FA-Y	62.8	C	24.4	29.9	3.4
FA-W	62.8	C	24.2	29.0	4.2
FA-V	62.9	C	24.8	29.4	8.5
FA-U	65.7	C	21.9	26.8	8.1
FA-B	67.7	C	14.3	17.8	15.7
FA-S	70.6	F	17.1	20.5	18.8
FA-R	73.2	F	15.3	20.6	1.8
FA-P	73.3	F	14.0	18.3	2.6
FA-Q	74.3	F	16.6	20.1	6.3
FA-T	77.4	F	13.6	16.6	10.6
FA-O	79.8	F	10.2	13.4	36.8
FA-M	81.9	F	7.17	9.8	6.2
FA-K	83.5	F	6.85	8.6	31.4
FA-L	84.8	F	6.79	7.6	12.3
FA-N	87.0	F	5.33	6.5	20.8
FA-E	87.8	F	2.78	4.0	35.9
FA-C	89.0	F	2.24	4.0	17.8
FA-I	89.5	F	1.81	3.1	34.6
FA-G	89.9	F	1.45	2.6	44.3
FA-F	90.7	F	1.09	1.9	46.8
FA-H	91.2	F	3.46	4.6	6.7
FA-J	91.9	F	1.28	2.3	28.3
FA-A	92.5	F	0.82	1.7	20.3

Moisture content and LOI tests are currently limited to a sample mass of 1 g. The small sample mass can affect the precision of the determinations particularly for test results of low magnitudes, as is the case when analyzing CFA; this deficiency could be eliminated by simply increasing the sample mass. LOI test results generally are not significantly influenced by the mass of the CFA sample as seen in Figure 4.14 for a fixed ignition time of 45 min at 720°C, with no reheat cycle. These results are likely because the determinations were made using porcelain crucibles, each having a mass of approximately 10 to 12 g. The LOI test can be further improved by removing the reheat cycle required by ASTM

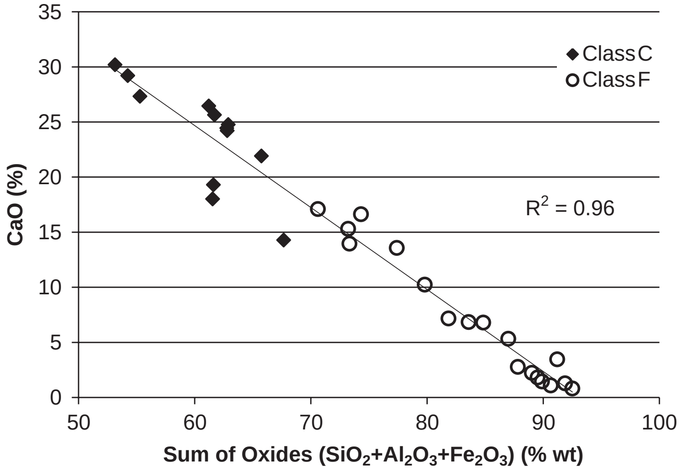

Figure 4.12. Correlation between CaO and the sum of the oxides.

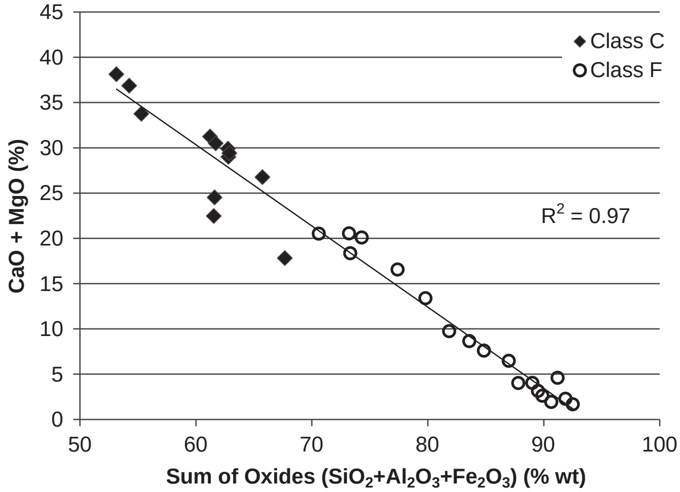

Figure 4.13. Correlation between CaO + MgO and the sum of the oxides.

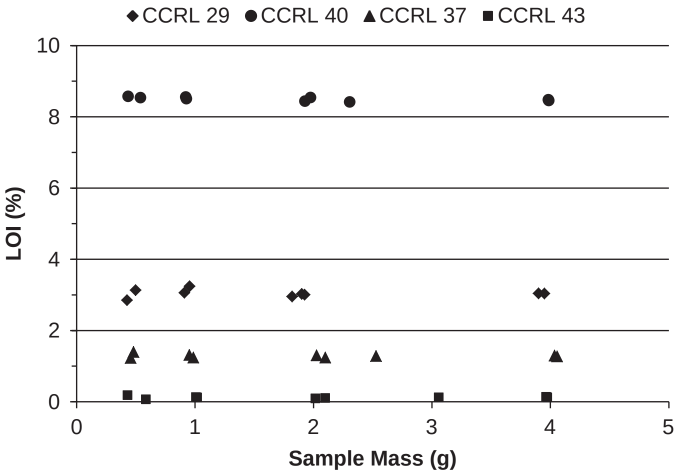

Figure 4.14. Influence of sample mass on %LOI.

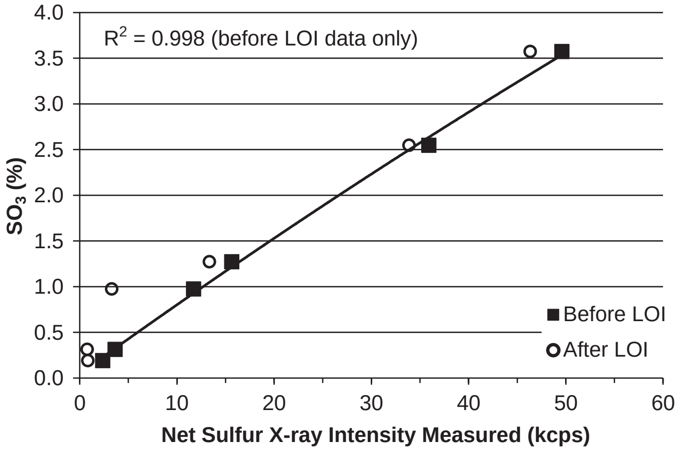

Figure 4.15. Sulfur loss during the LOI test.

C114, which is very time consuming when working with porcelain crucibles that cool much slower than platinum crucibles typically used with cement. Coal fly ash may contain a significant amount of carbon that can destroy platinum crucibles.

The thermal analysis experiments clearly indicated most CFA samples lost mass but some samples gained small amounts of mass unrelated to the carbon content of the sample. All the thermal gravimetric analysis curves indicated that the CFA samples started to rapidly lose mass at 500°C to 600°C and then remained relatively stable up to approximately 900°C. Additional discussion of the thermal analysis is presented in Appendix C.

Sulfur (SO_3) determination tests indicated that values obtained from the fused disk technique tended to be in very poor agreement with SO_3 values determined using pressed pellets, particularly for Class F fly ash that had LOI greater than 1% and total SO_3 values less than 1%. However, test results were within the specification limit but with large differences between labs. Because it is common practice to use a portion of the ignited sample (i.e., constant mass) obtained from the LOI test to manufacture fused disks for XRF analysis, analysts need to be aware of this potential error. Further tests indicated the majority of the sulfur was lost during the LOI test, as shown in Figure 4.15.

CFA Pozzolanic Reactivity

SAI Tests

Conventional SAI and PAI tests were performed on all 30 CFA sources and also using an inert filler. These tests indicated an inert material could meet SAI test requirements. To explore improvements to the SAI and PAI tests, a series of modified tests were conducted. These included an SAI test performed with 20% and 35% by weight replacement of cement with the quartz filler (INF-1). In addition to the higher substitution rates, all specimens were prepared using a constant *w/cm* rather than a constant flow. Because fly ash particles generally increase the flow of a mortar due to their spherical shape, a reduction in water content was necessary to maintain a constant flow, which potentially enables a non-pozzolanic fly ash to meet the SAI requirements in AASHTO M 295. Strengths and SAI values using the inert filler are shown in Table 4.13.

Table 4.13 shows that mortars containing 20% replacement of cement with non-pozzolanic ground quartz filler met or exceeded the AASHTO M 295 SAI requirement (i.e., 75%) at both 7 and 28 days, even at a constant *w/cm* ratio. This result is likely due to the effect of a filler on nucleation and acceleration of cement hydration. This ground quartz would meet the SAI requirements for a Class F fly ash despite not having any pozzolanic value. However, at a replacement level of 35%, this non-pozzolanic filler did not meet the 75% limit at either 7 or 28 days.

For evaluating the SAI and KHI tests, the effect of different quartz fillers was investigated. The compressive strength of ASTM C109 mortar cubes made with quartz filler INF-1 were compared to that obtained using INF-2 quartz filler; results are shown in Figure 4.16. At a 20% replacement of cement, there was a negligible difference in strength between the mortars prepared with either cement type or inert filler, with the exception of a lower 28-day strength for the PC-2 and INF-1 combination. At a 35% replacement of cement, the effect of filler type was more pronounced when PC-2 was compared with PC-3, with INF-1 mortars having higher strengths than comparable INF-2 mortars.

The modified SAIs for eight CFAs at 20% replacement are presented in Table 4.14. The SAIs for four Class C CFAs at 35% replacement are presented in Table 4.15.

Table 4.13. Strengths and SAI for the INF-1 filler at 20% and 35% cement replacement.

Cement Type	Age (Days)	100% Cement	20% Replacement		35% Replacement	
		Strength (psi)	Strength (psi)	SAI	Strength (psi)	SAI
PC-1	7	4,554	3,829	84	3,075	68
PC-2	7	4,293	3,408	79	2,640	62
PC-3	7	4,090	3,539	87	2,886	71
PC-1	28	5,715	4,815	84	3,945	69
PC-2	28	5,526	4,235	77	3,655	66
PC-3	28	5,134	4,351	85	3,307	64

The tests conducted to evaluate whether the SAI and PAI indicate the minimum strength level, CFA replacement level, or both need to be modified so that inert materials will not meet the specification requirements.

KHI Tests

Results of the KHI tests are shown in Table 4.16 for the three cements and 20% replacement by the eight CFAs, and 35% replacement by the four Class C CFAs, at 7, 28, and 56 days. As indicated by the negative values, fly ashes FA-H and FA-O had 7-day strengths lower than obtained with the INF-1 filler. These results indicate the pozzolanic reaction of FA-H and FA-O did not lead to strength gain at 7 days but were likely acting as a filler and providing nucleation sites for hydration of cement. This demonstrates the KHI test's ability to separate filler effects from pozzolanic contributions.

The SAI versus KHI values at 7 days of age are presented in Figures 4.17 and 4.18 for 20% and 35% CFA replacement of cements, respectively; the values at 56 days of age are presented in Figures 4.19 and 4.20, respectively. As can be seen, the two tests appear to provide similar prediction of strength development. However, the KHI values range from approximately 0 (for inert materials) to over 100% (equal performance to the cement).

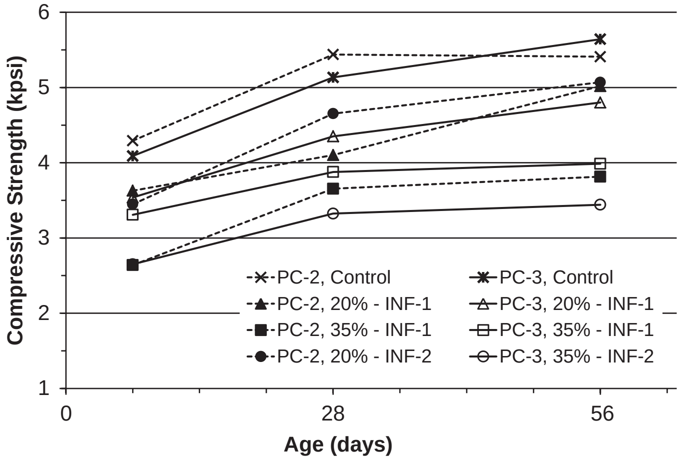

Figure 4.16. Cube strengths for different fillers, cements, and replacement levels.

Figures 4.21 and 4.22 show the SAI and KHI values versus compressive strength for combinations of eight CFA sources and three cements. These figures show that both methods provide a similar trend for strength development. Also both methods indicate a clear effect of cement type with both PC-2 and PC-3 yielding higher values of SAI and KHI than PC-1 for the same CFA.

Effect of Carbon on Air Entrainment

To evaluate the application of the developed tests for assessing the effects of CFA on air entrainment, tests were performed and correlated with known LOI values for the various CFAs,

Table 4.14. Strength activity indices of coal fly ashes at 20% replacement.

	7-Day SAI			28-Day SAI			56-Day SAI		
	Cement			Cement			Cement		
ID	PC-1	PC-2	PC-3	PC-1	PC-2	PC-3	PC-1	PC-2	PC-3
FA-H	79	80	81	95	98	95	92	108	98
FA-M	85	85	90	103	89	90	93	106	90
FA-O	85	78	83	85	94	91	91	98	86
FA-Q	92	88	90	106	100	101	104	111	104
FA-U	103	88	98	113	94	111	107	108	95
FA-X	102	100	97	99	84	96	106	103	99
FA-ZA	103	89	101	113	100	108	110	104	88
FA-ZC	117	96	92	106	104	105	108	112	101

Table 4.15. Strength activity indices of Class C coal fly ashes at 35% replacement.

	7-Day SAI			28-Day SAI			56-Day SAI		
	Cement			Cement			Cement		
ID	PC-1	PC-2	PC-3	PC-1	PC-2	PC-3	PC-1	PC-2	PC-3
FA-U	87	70	81	101	81	97	107	101	109
FA-X	96	90	103	106	89	98	92	105	94
FA-ZA	93	75	89	107	82	105	106	101	100
FA-ZC	113	79	82	95	92	94	101	100	99

Table 4.16. Keil hydraulic indices for 20% and 35% CFA replacement of cements and using filler INF-1.

	7-day KHI (%)			28-day KHI (%)			56-day KHI (%)		
ID	**PC-1**	**PC-2**	**PC-3**	**PC-1**	**PC-2**	**PC-3**	**PC-1**	**PC-2**	**PC-3**
20% Replacement									
FA-H	−31	4	−43	71	91	66	60	162	88
FA-M	7	28	26	119	55	34	66	143	50
FA-O	10	−6	−24	7	73	39	57	84	26
FA-Q	53	44	26	135	102	109	120	185	121
FA-U	121	40	84	184	75	171	133	158	73
FA-X	115	101	80	96	30	72	127	126	96
FA-ZA	122	46	110	184	99	153	150	132	38
FA-ZC	203	83	41	138	119	130	140	193	106
35% Replacement									
FA-U	60	21	35	102	44	93	121	102	126
FA-X	89	74	110	118	68	94	78	114	82
FA-ZA	80	35	63	124	46	114	116	102	101
FA-ZC	140	45	39	83	75	82	102	99	96

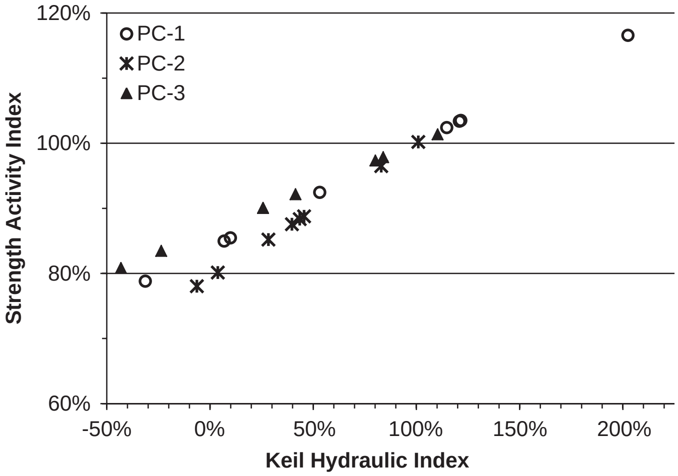

Figure 4.17. SAI versus KHI values at 7 days for a 20% replacement level.

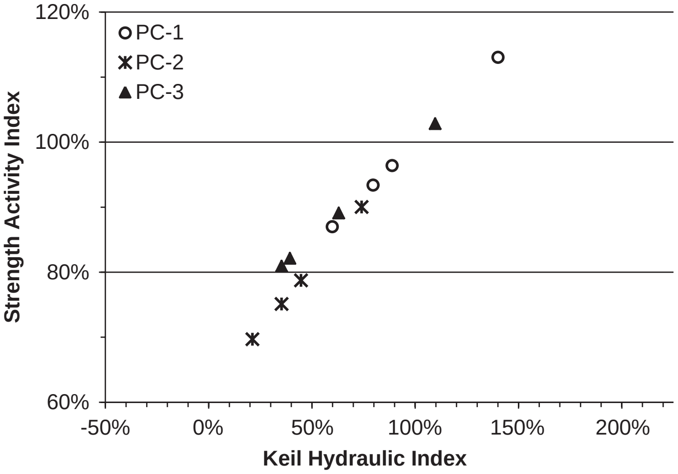

Figure 4.18. SAI versus KHI values at 7 days for a 35% replacement level.

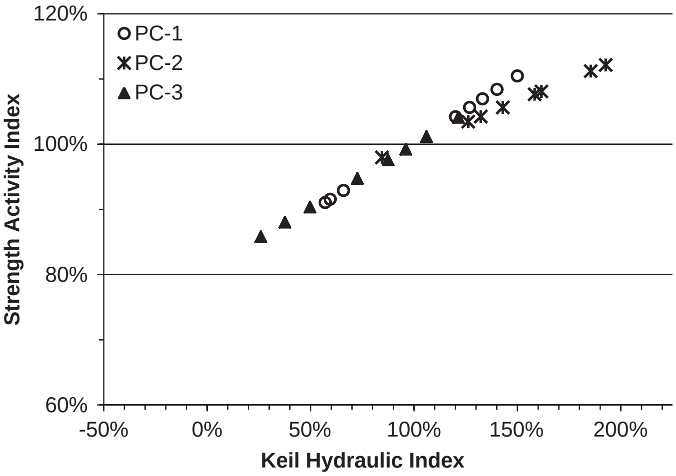

Figure 4.19. SAI versus KHI values at 56 days for a 20% replacement level.

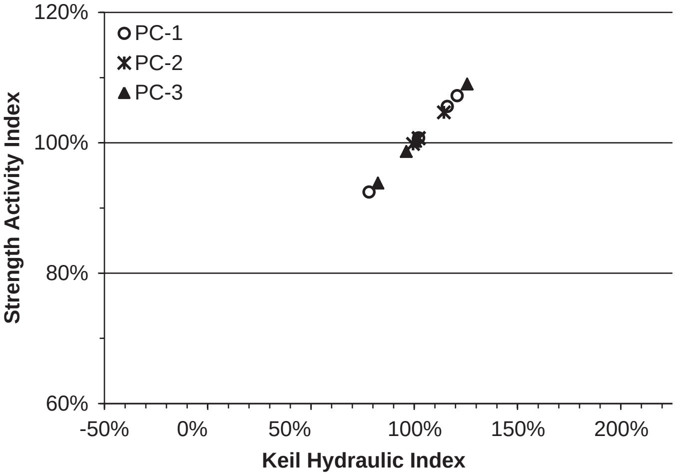

Figure 4.20. SAI versus KHI values at 56 days for a 35% replacement level.

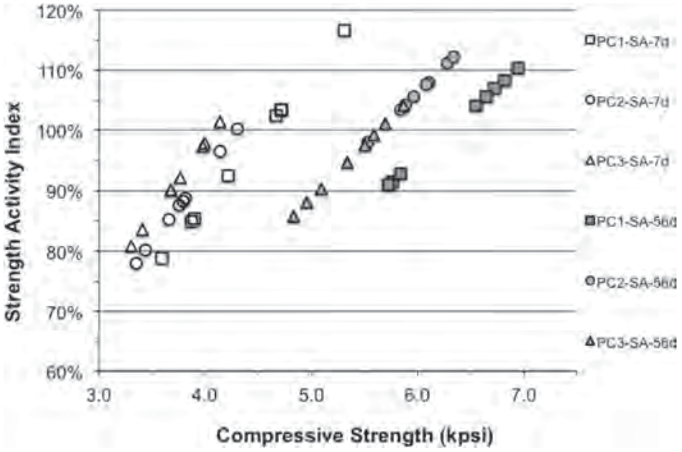

Figure 4.21. SAI versus compressive strength values for a 20% replacement level.

and also correlated with each other. Also, a series of mortar and concrete mixtures were prepared to demonstrate the application of the various tests. Key results are summarized here; additional results are presented in Attachment C.

Correlation among the Tests

Foam Drainage Test

Test results indicated that in most cases, the foam drainage test does not adequately characterize the interaction of AEAs with CFAs having significantly different levels of LOI. The high ratio of AEA to water used in the test may explain the similarity in results obtained with different CFAs. Published results for the foam drainage test use cementitious combinations (i.e., CFA plus cement). The test was ineffective in evaluating the impact of fly ash only.

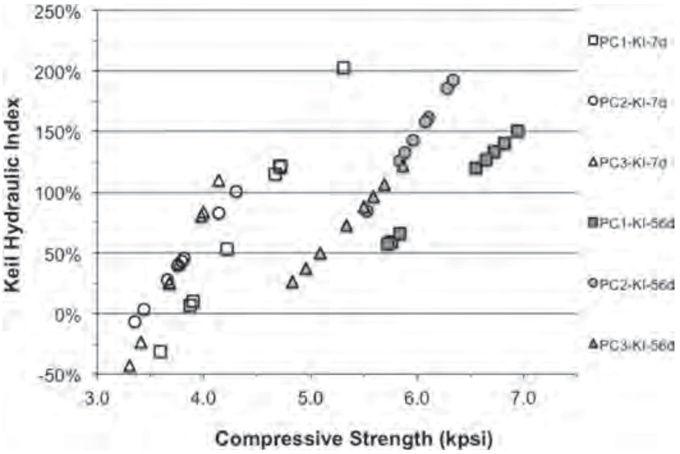

Figure 4.22. KHI versus compressive strength values for a 20% replacement level.

Foam Index Test

An example of the correlation between the measured foam index number and LOI is shown in Figure 4.23. Relationships for the six principal AEAs tested and the numeric results are summarized in Attachment C.

The relationship between LOI and the foam index test is reasonable but the variability in the results is high compared to the results from either the CFA iodine number or the direct adsorption isotherm tests. One source of this variability is the subjective nature of the test. Also, for some fly ash sources there is anomalous behavior with respect to correlation between the foam index test and the LOI results. Another source of variation is that LOI measures the mass of carbon and does not account for the adsorption potential of the carbon.

The foam index test is fundamentally different from the iodine and direct isotherm tests. For the latter two tests, a CFA is equilibrated with a high concentration of adsorbate (relative to the foam index test). However, in the foam index test, the system starts with no adsorbate and then AEA (i.e., adsorbate) is introduced in an incremental manner. The AEA concentration increases from zero until a stable foam is formed but equilibrium conditions may never be achieved. The foam index test is dynamic and if the system was left to equilibrate, the foam might likely disappear because adsorption continues to take place. In comparison, isotherms are based on equilibrium conditions after which no significant change in the concentration occurs.

CFA Iodine Number Test

CFA iodine number tests were performed on 14 CFA sources and the results are summarized in Table 4.17.

The CFA iodine number versus LOI is shown in Figure 4.24, which presents a linear relationship. Figure 4.25 presents the

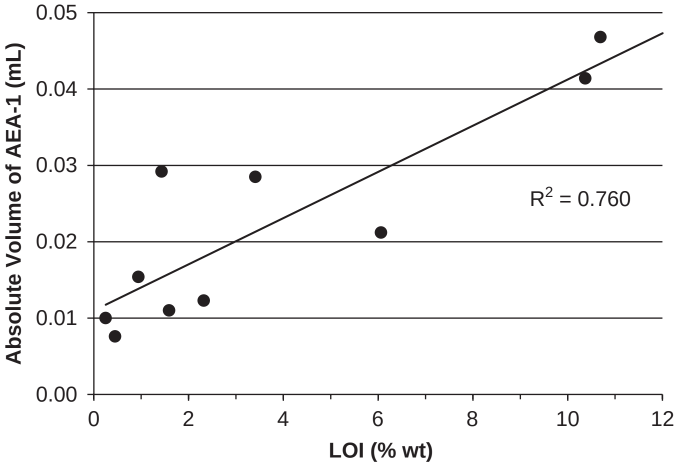

Figure 4.23. Absolute volume of AEA added (mL) versus measured LOI.

Table 4.17. Results of CFA iodine number test.

ID	LOI (%)	Iodine No. (mg/g CFA)
FA-H	0.25	0.004
FA-T	0.45	0.001
FA-A	0.94	0.013
FA-J	1.59	0.545
FA-O	1.43	0.535
FA-G	2.32	0.354
FA-ZN	3.41	2.619
FA-ZF	6.06	3.761
25-75 Blend*	10.37	10.989
FA-ZM	10.69	7.266
50-50 Blend*	14.68	16.857
75-25 Blend*	18.99	25.205
FA-ZJ	21.34	35.603
FA-ZE	23.30	30.583

*FA-ZF/FA-ZE blends

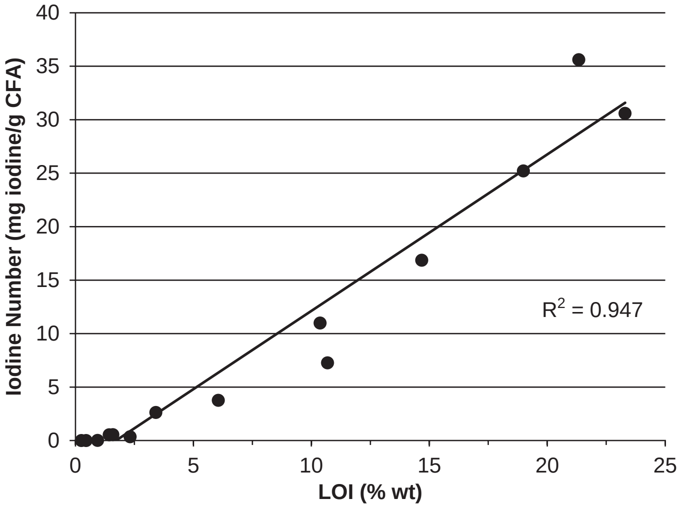

Figure 4.24. CFA iodine number versus LOI.

iodine number versus LOI on a semi-log plot for the same CFA sources. This figure highlights the ability of the test to detect differences in adsorption for relatively low LOI ashes. For example, FA-T (LOI = 0.45%) has a higher LOI than FA-H (LOI = 0.25%), yet FA-H exhibited a higher CFA iodine number (i.e., adsorption); a similar observation can be made for FA-J, FA-O, and FA-G. This observation can be attributed to the nature of the LOI test because many factors, such as decomposition of carbonate minerals (e.g., $CaCO_3$) and portlandite [$Ca(OH)_2$] and combustion of carbon affect the mass loss of fly ash as a result of burning. Also, a gain in mass may occur due to the oxidation of sulfur and iron. CFA sources with the same LOI may have different adsorption properties depending on the form of available carbon. For high LOIs, the majority of the mass loss is due to carbon volatilization and therefore errors with the LOI test tend to be high at lower LOI values.

Direct Adsorption Isotherm Test

The final evaluation of the direct adsorption isotherms was conducted on six AEAs (AEA-1 through AEA-6 in Table 3.2) and eight CFAs listed in Table 3.1.

Adsorption isotherms for eight CFAs and AEA-1 are presented in Figure 4.26 and in Attachment C for the other five AEAs. These isotherms quantify the amount of AEA adsorbed by the CFA as a function of the AEA concentration.

The AEA solution concentration in the cement-only mixture is determined by dividing the volume of AEA in the mixture by the volume of water used in the concrete mixture. The CFA adsorption capacity at this concentration can then be determined from the isotherm graph. For example, the adsorption capacity of FA-T (LOI = 0.45%) for AEA-1 at an initial concentration (C_0) of 0.3% volume of AEA is 0.0023 mL of AEA per gram of

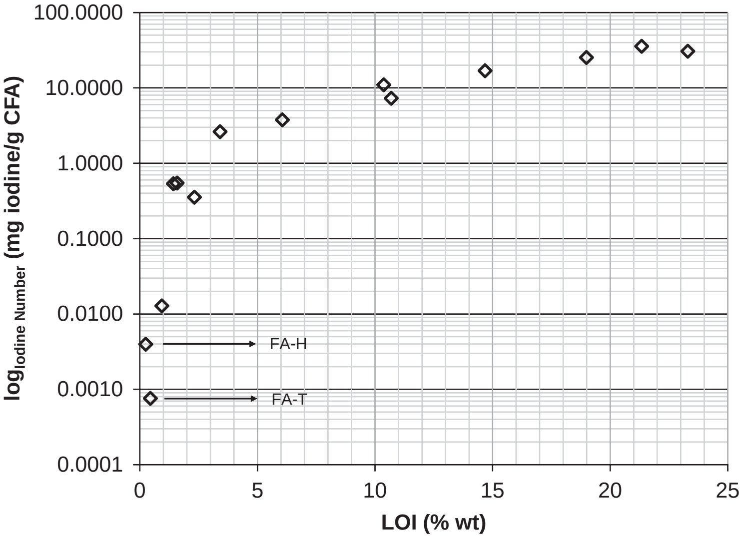

Figure 4.25. CFA iodine number versus LOI (on a semi-log scale).

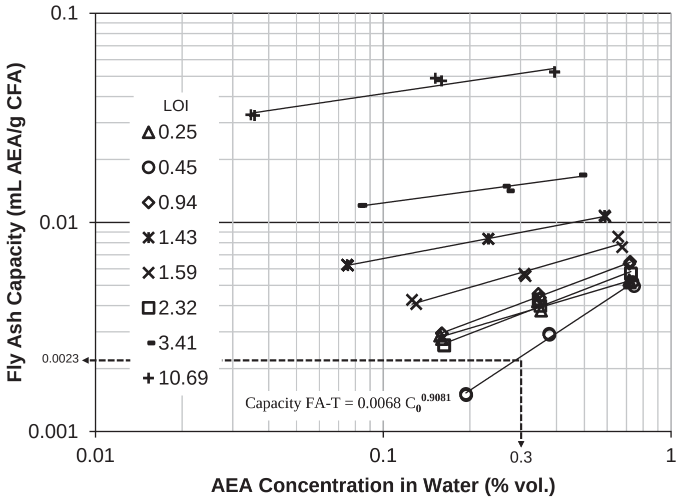

Figure 4.26. Adsorption isotherms of AEA-1 with eight coal fly ashes.

CFA (Figure 4.26). This capacity multiplied by the total mass of CFA in the mixture determines the volume of AEA-1 adsorbed by FA-T for the specified initial concentration. The capacity is the first estimate of the correction to the initial AEA dosage (i.e., cement-only mixture) to compensate for the adsorption of AEA-1 by FA-T. As shown in Figure 4.26, the capacity can be determined graphically or by fitting a power line to the isotherm points and determining the Freundlich equation coefficients.

LOI Correlation to Adsorption Tests

Table 4.18 and Figure 4.27 illustrate the relationship between LOI and the CFA iodine number, foam index, and CFA capacity measured by direct adsorption isotherms. The foam index and adsorption isotherm tests in Figure 4.27 are performed with AEA-1 at a concentration of 0.4% vol. Similar relationships for AEA-1 through AEA-6 are provided in Attachment C.

Figure 4.27 shows the correlation of all adsorption-based tests to LOI for AEA-1. The foam index test shows the most deviation and scatter but generally correlates with the other results. However, the LOI does not provide a good correlation to adsorption capacity for many of the CFAs with a moderate level of LOI (FA-O LOI = 1.43% and FA-G LOI = 2.32%). All three adsorption-based tests show FA-G has less adsorption capacity than FA-O suggesting the LOI value does not reflect the true adsorption potential of the CFA. The same is true for FA-H (LOI = 0.25%) and FA-T (LOI = 0.45%) where FA-H has a higher capacity than FA-T as shown by the three adsorption-based tests. These observations agree with an earlier finding that, depending on the composition of the CFA, using LOI as a measure of carbon content could be as accurate as 99% or have as much as a 75% error between carbon content and LOI (Brown and Dykstra, 1995). Based on these results, it appears that LOI is not a reliable test for predicting AEA adsorption, particularly for lower-carbon-content CFAs because the non-carbon-related mass change can be a significant fraction of the reported LOI while not affecting the adsorption behavior of the CFA. However, LOI provides a good indication of carbon content, and therefore adsorption capacity, for high-carbon CFAs, because the loss in mass due to burning carbon is substantially higher than the mass loss/gain by other mechanisms.

The iodine number test assesses the adsorption properties of a CFA using iodine as an adsorbate; it does not measure AEA adsorption but classifies the CFA in terms of its performance as an adsorbent. The difference in adsorption capacity for a given CFA is dependent upon the AEA. The direct adsorption isotherm test measures the adsorption of AEA for a specific AEA and CFA combination, which can be expressed as a function of the CFA iodine number. The foam index test measures a physical property of the AEA-water solution that is affected by the adsorption of AEA from that solution, which can be expressed in terms of either the CFA iodine number or the direct adsorption isotherm. Any one of these tests can predict the effect of CFA addition on air entrainment in concrete by measuring

Table 4.18. LOI, foam index, CFA capacity, and CFA iodine number.

ID	LOI (%)	Foam Index* (mL)	Capacity* (mL/g CFA)	CFA Iodine No. (mg I/g CFA)
FA-H	0.25	0.01	0.004125	0.00397
FA-T	0.45	0.0076	0.002959	0.00076
FA-A	0.94	0.0154	0.004737	0.01279
FA-O	1.43	0.0292	0.009677	0.53464
FA-J	1.59	0.011	0.006458	0.54499
FA-G	2.32	0.0123	0.004244	0.35415
FA-ZN	3.41	0.0285	0.016040	2.61915
FA-ZM	10.69	0.0468	0.054647	7.26624

* Determined for AEA-1

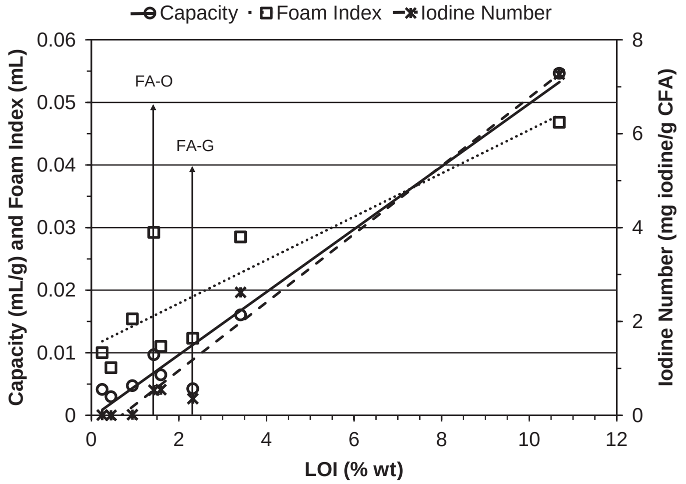

Figure 4.27. LOI correlations to CFA iodine number, foam index, and CFA capacity for AEA-1.

adsorption properties—not the physical property of LOI that may or may not correlate to adsorption capacity.

Foam Index Test Correlation to Adsorption Tests

The foam index test, in its improved form where the total time of the test is consistent, provides a better representation of the adsorption capacity of CFA than LOI. Figure 4.28 presents a comparison between the foam index test results, direct adsorption measurements for AEA-1, and the CFA iodine number for eight CFAs. The results, although more variable, show the foam index test provides a clear trend following the CFA iodine number and correlating to adsorption capacity. The CFA iodine number test results correlate better with adsorption capacity measurements than the foam index test results because of the low resolution, non-equilibrium conditions, and the subjective nature of the foam index test.

CFA Iodine Number Correlation to Direct Adsorption Isotherms

The CFA iodine number is a measure of the capacity of CFA for iodine. Iodine is a single solute and has a much smaller molecular size than a typical AEA and is easily adsorbed onto carbon. Figure 4.29 illustrates the relationship between direct adsorption isotherms and CFA iodine number for AEA-5 and eight CFA sources. Figure 4.30 shows the CFA iodine number and AEA adsorption capacity for several AEAs. The figure shows that the relative adsorption affinity of each AEA can be established with the lowest capacity at a given iodine number being the AEA with the least tendency to adsorb.

The figure also shows, for iodine numbers below 0.1 mg/g, the AEA adsorption capacity is low and does not vary significantly over this CFA iodine number range. For CFA iodine number values between 0.1 and 1, the AEA capacity begins to rapidly increase in magnitude. CFA iodine numbers greater than 1 indicate a very significant level of adsorption and the adsorption capacity increases with small changes in the CFA iodine number. This relationship can be used in modifications of CFA specifications.

The relationships shown in Figures 4.29 and 4.30 illustrate a simple means for determining the capacity of a CFA based on the iodine number. By selecting a suite of CFAs with varying adsorption potential and determining the CFA capacity based on the direct adsorption isotherm test for a given AEA, as well as determining the iodine number for those CFAs, a plot similar to Figure 4.29 would be generated. The user would then determine adsorption capacity for the AEA corresponding to the iodine number for the CFA. For example, if AEA-5 (as

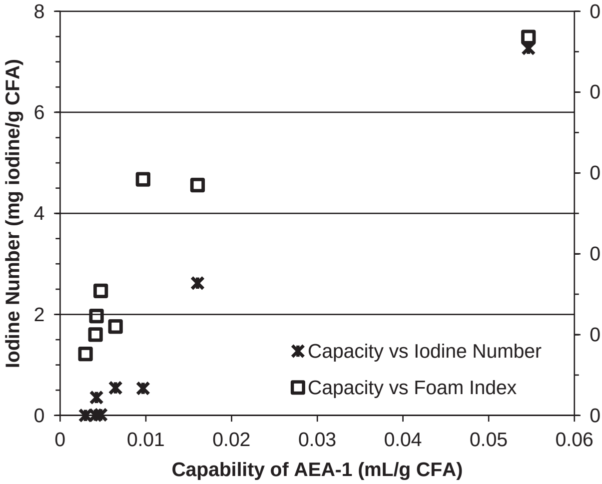

Figure 4.28. Relationship between CFA iodine number and foam index test versus capacity of AEA-1.

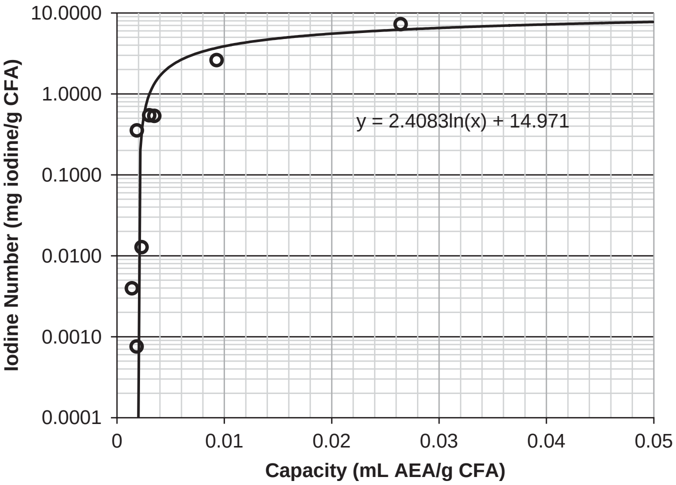

Figure 4.29. Relationship between CFA iodine number and direct adsorption isotherm capacity for AEA-5.

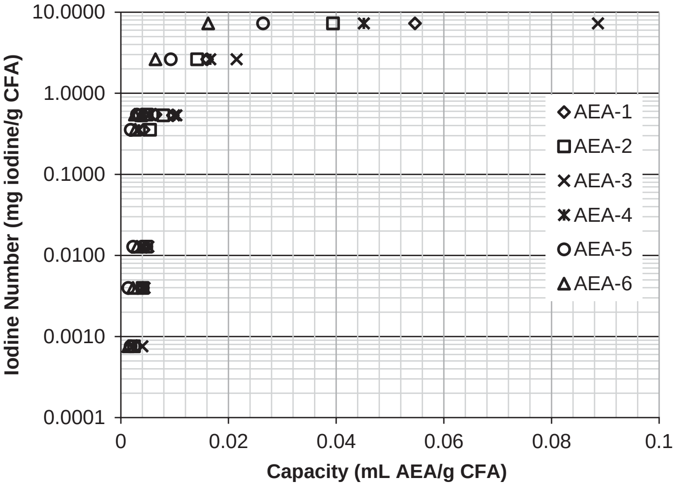

Figure 4.30. Relationship between CFA iodine number and direct adsorption isotherm capacity for six AEAs and eight CFA sources.

shown in Figure 4.29) is used with a CFA that has an iodine number of 3, the capacity of that CFA for AEA-5 would be approximately 0.01 mL/g of CFA.

Correlation with Mortar and Concrete

Mortar Experiments

Application of the direct adsorption isotherm test for predicting the adjustment to AEA dosage was investigated using cement-only control mixtures and separate batches of cement and fly ash mixtures. The AEA dosage was determined by (1) trial and error and (2) using the direct adsorption isotherm; the results are shown in Figures 4.31 through 4.36. The air contents of cement-only control mixtures are shown as "Baseline Air Content." The error bars indicate the range in air content obtained with 16 repetitions (i.e., 17 total batches) of each mixture combination. The variability in air content obtained in the control mixtures was typically ±1.5% to 2% total air content.

The AEA dosages determined using the trial-and-error approach are listed in Table 4.19 and the dosages determined using the direct adsorption isotherm test are presented in Table 4.20. Table 4.21 shows the change in the AEA dosages from the baseline dosages.

Test results show that if the mixtures made using AEA-5 are disregarded, in 73% of the cases, the air content obtained by the two approaches agree within ±1.5% to 2% total air content of the baseline air content. FA-ZM, an extremely high LOI material (LOI = 10.69% wt), was included to investigate the use of the direct adsorption isotherm test for these materials. In spite of the high adsorption capacity of this ash, predictions for two of the five AEAs (excluding AEA-5) were within the margin of error and one estimate was slightly outside this range.

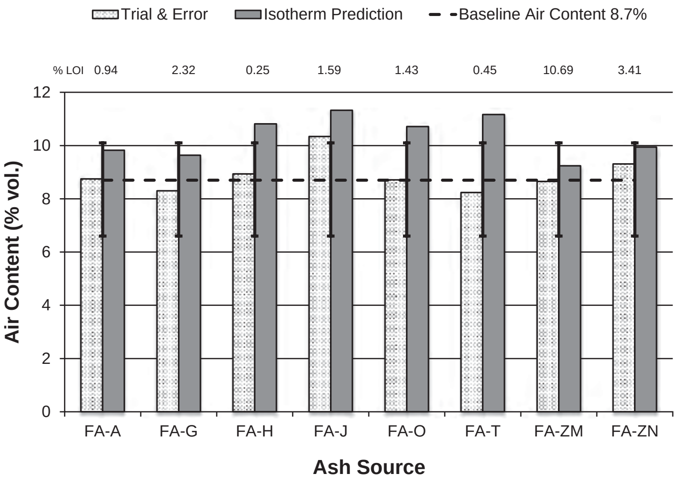

Figure 4.31. Air contents for mortar mixtures with AEA-1.

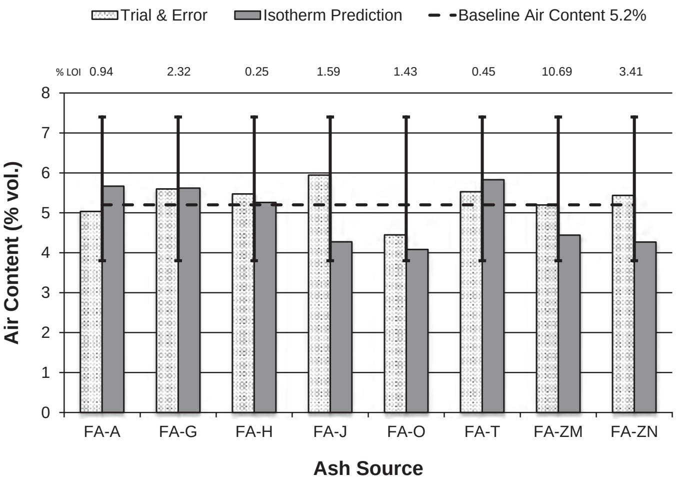

Figure 4.32. Air contents for mortar mixtures with AEA-2.

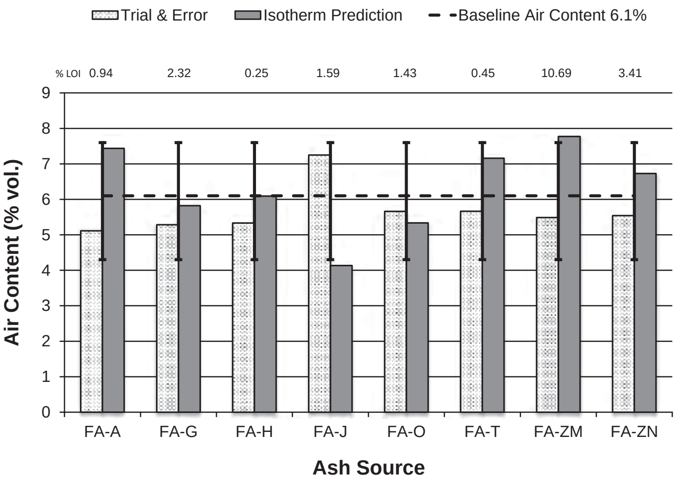

Figure 4.33. Air contents for mortar mixtures with AEA-3.

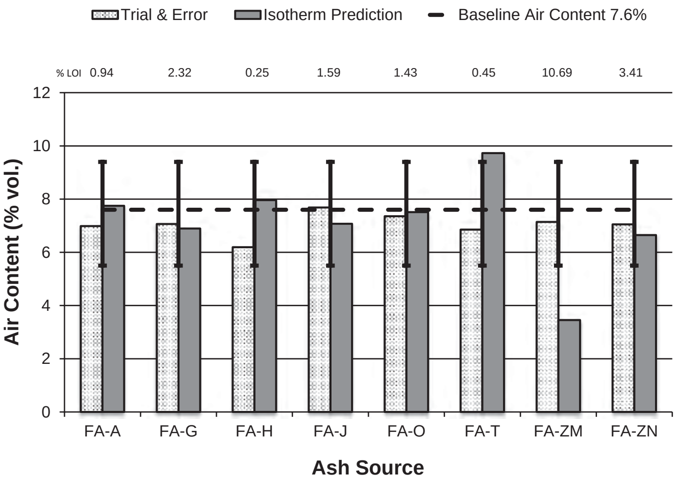

Figure 4.34. Air contents for mortar mixtures with AEA-4.

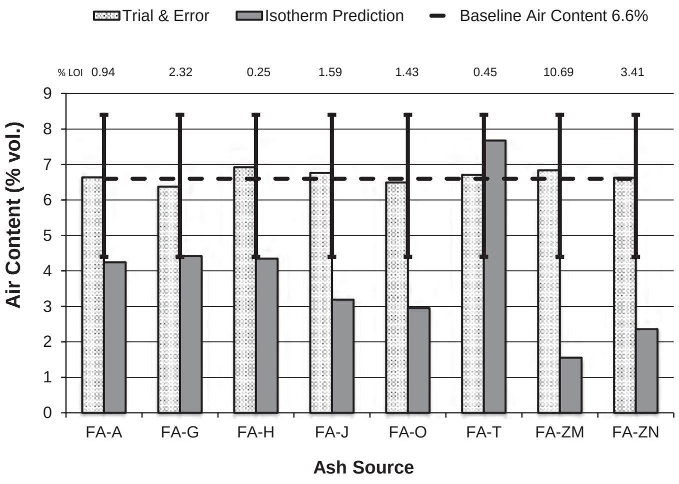

Figure 4.35. Air contents for mortar mixtures with AEA-5.

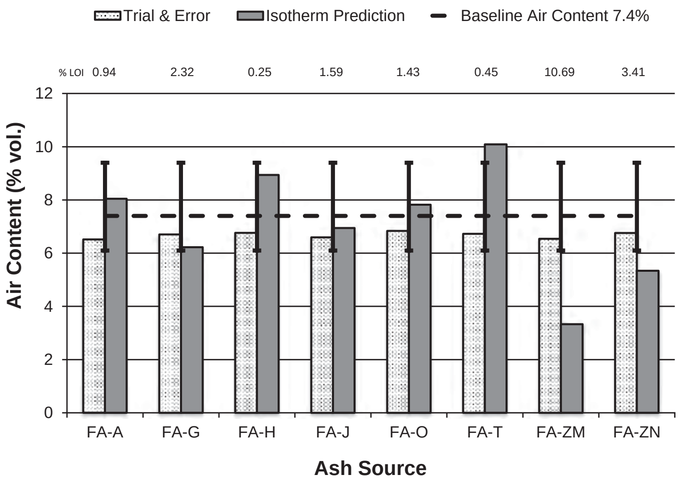

Figure 4.36. Air contents for mortar mixtures with AEA-6.

Figure 4.35 shows the direct adsorption isotherm test did not accurately predict the adsorption of AEA-5 with any of the CFAs; the required dosage to achieve the target air content was twice the manufacturer's recommended maximum for cement-only control mixtures (Table 3.5). Direct adsorption isotherms were performed for AEA-9 (a benzene sulfonate). A series of control mortars were prepared using AEA-9 and PC-1 to determine a baseline dosage (i.e., 1.15 oz/cwt and 7.4% vol. air). The trial-and-error approach and the direct adsorption isotherm test were used to determine AEA-9 dosages for CFA mortar mixtures with FA-J and FA-O; the results are summarized in Table 4.22. The values shown for the air content obtained by trial and error were measured while the values shown for the air content obtained using the direct adsorption isotherm were predicted from the AEA dosage versus air content relationship established by trial and error.

The variability of these control mixtures was not established but is assumed to be similar to the other control mortar mixtures (i.e., ±1.5% to 2% vol. air). With this variability, the predicted air content for the FA-J mixture was near the limits of variation and the predicted air content for the FA-O mixture was almost identical to that determined by trial and error for mortar mixtures.

The data presented in Table 4.21 show that changes in dosage for FA-T (a borderline Class C/Class F ash with low LOI) mixtures between the baseline dosages and those determined empirically were quite small or negative, which is common with Class C ashes. However, neither adsorption-based tests nor existing LOI testing predicted a decrease in AEA dosage.

CFA sources FA-A, FA-G, and FA-H represent beneficiated ashes: FA-A is a triboelectrostatic processed ash, FA-G is a carbon burn-out ash, and FA-H an air classified ash. The air content for mortars prepared using the change in dosage predicted by the direct adsorption isotherm fell within the margin of error in 93% (i.e., 14/15) of the cases (excluding AEA-5). These ashes represent the type of fly ash that may become more common in the future.

Although FA-A and FA-G are processed to remove carbon, there was still a significant increase in AEA demand for these CFA sources, likely because removal of carbon from CFA may be based on lowering the measured LOI and not the bulk adsorption potential. The processes used likely will remove larger carbon particles first, thereby lowering the LOI of the ash. However, the smaller carbon particles contribute most to AEA adsorption due to their high specific surface and these carbon particles can impact AEA demand

Table 4.19. AEA dosages based on the trial-and-error approach.

		AEA Dosage (oz AEA/cwt cementitious)					
Baseline Dosage		*2.12*	*0.81*	*0.61*	*1.77*	*1.84*	*1.54*
ID	**LOI**	**AEA-1**	**AEA-2**	**AEA-3**	**AEA-4**	**AEA-5**	**AEA-6**
FA-A	0.94	4.24	2.24	1.84	5.30	5.07	1.54
FA-G	2.32	4.24	2.04	1.07	2.65	3.96	3.07
FA-H	0.25	3.18	1.63	1.23	6.18	4.61	3.07
FA-J	1.59	3.44	2.24	2.00	3.53	5.07	1.92
FA-O	1.43	4.13	2.64	3.68	5.47	5.99	3.07
FA-T	0.45	1.80	0.94	0.61	1.32	2.30	0.77
FA-ZM	10.69	20.13	15.87	62.02	107.69	37.30	13.05
FA-ZN	2.41	7.94	6.92	5.83	9.71	11.97	5.37

Table 4.20. AEA dosages based on the direct adsorption isotherm test.

		AEA Dosage (oz AEA/cwt cementitious)					
Baseline Dosage		*2.12*	*0.81*	*0.61*	*1.77*	*1.84*	*1.54*
ID	**LOI**	**AEA-1**	**AEA-2**	**AEA-3**	**AEA-4**	**AEA-5**	**AEA-6**
FA-A	0.94	3.66	1.55	1.18	2.98	2.39	2.26
FA-G	2.32	3.49	1.69	0.88	2.80	2.26	2.19
FA-H	0.25	3.51	1.38	1.08	3.11	2.13	2.12
FA-J	1.59	4.30	1.69	1.09	3.32	2.55	2.28
FA-O	1.43	5.53	2.54	1.82	4.96	2.69	2.70
FA-T	0.45	2.97	1.08	1.03	2.42	2.24	1.86
FA-ZM	10.69	21.76	11.12	21.26	16.98	8.06	6.62
FA-ZN	2.41	7.92	4.49	4.45	7.52	4.47	3.55

Table 4.21. The relative change in AEA dosage from the baseline dosages.

		Percentage Change in AEA Dosage					
ID	**LOI**	**AEA-1**	**AEA-2**	**AEA-3**	**AEA-4**	**AEA-5**	**AEA-6**
FA-A	0.94	100	176	200	200	175	0
FA-G	2.32	100	151	75	50	115	100
FA-H	0.25	50	100	100	250	150	100
FA-J	1.59	63	176	225	100	175	25
FA-O	1.43	95	225	500	210	225	100
FA-T	0.45	−15	15	0	−25	25	−50
FA-ZM	10.69	850	1,851	10,000	6,000	1,925	750
FA-ZN	2.41	275	751	850	450	550	250

Table 4.22. AEA dosages and air contents for mortar mixtures with AEA-9.

CFA ID	AEA Dosage (oz/cwt)			Air Content (% vol.)		
	Baseline	**Trial & Error**	**Direct Adsorption Isotherm**	**Baseline**	**Trial & Error**	**Direct Adsorption Isotherm (Predicted)**
FA-J	1.15	1.74	2.59	7.40	7.44	8.96
FA-O	1.15	2.93	3.05	7.40	7.45	7.49

significantly. As processing is adapted to remove carbon from CFA, it will be increasingly important to measure the efficacy of that process with respect to its impact on AEA adsorption, not LOI. The CFA iodine number and direct adsorption isotherm tests are new approaches to quantify AEA adsorption by CFA.

Concrete Experiments

The purpose of the concrete experiment was to provide additional evaluation of the direct adsorption isotherm test. Control mixtures were prepared with an air content of 6.5% ± 1.5% (AEA dosage was determined by trial and error); the results are listed in Table 4.23.

For the test mixtures with 25% fly ash, the AEA dosage used was based on the results for mortars that used the same combination of AEA and CFA. For example, if a particular CFA-AEA combination required a 50% larger AEA dosage compared to that required for a mortar mixture, then a 50% increase was applied to the AEA dosage for the concrete mixtures of the same combination. The estimated dosages are listed in Table 4.23 for the control mixtures and those with 25% CFA.

As seen in Table 4.23, the trial-and-error results for mortar were successfully used to predict AEA dosages for concrete, except when AEA-1 is used with mixtures containing FA-ZM (LOI = 10.69%) and FA-O (LOI = 1.43%). The differences with FA-ZM were not unexpected because of the high LOI content and AEA-1 was shown to be one of the most adsorbable AEAs.

Selected concrete mixtures were prepared using the direct adsorption isotherm test results to correct the baseline AEA dosage determined for concrete. As was done with the mortar mixtures, the adsorption capacity determined by the direct

Table 4.23. AEA dosages and air contents for concrete test mixtures.

AEA	Cementitious	AEA Dosage (oz/cwt)	Total Air Content (% vol.)
AEA-1	PC-1 Control	1.9	6.9
	PC-1 + 25% FA-A	3.8	6.9
	PC-1 + 25% FA-G	3.8	8.1
	PC-1 + 25% FA-O	3.7	3.9
	PC-1 + 25% FA-ZM	18.2	3.4
	PC-1 + 25% FA-ZN	7.2	5.4
AEA-2	PC-1 Control	1.7	5.8
	PC-1 + 25% FA-A	4.2	5.6
	PC-1 + 25% FA-G	4.6	6.5
	PC-1 + 25% FA-O	5.5	6.3
	PC-1 + 25% FA-ZM	32.9	5.4
	PC-1 + 25% FA-ZN	14.3	5.9
AEA-6	PC-1 Control	2.1	7.1
	PC-1 + 25% FA-A	4.3	5.5
	PC-1 + 25% FA-G	2.1	7.6
	PC-1 + 25% FA-O	3.1	6.8
	PC-1 + 25% FA-ZM	18.3	5.5
	PC-1 + 25% FA-ZN	7.5	6.5

adsorption isotherm test and the known weight of CFA in the concrete mixtures was used to determine an adjusted AEA dosage. The results, shown in Table 4.24, indicate that the direct adsorption isotherm estimation produced an air content within the desired range in nine of twelve cases (i.e., 75%).

There are many factors that affect air entrainment in concrete (e.g., mixing time, temperature, aggregate type), and there is significant variance in the ability to measure the air content in fresh concrete. The direct adsorption isotherm test only addresses the issue of AEA adsorption; in some cases, other factors will dominate. Nevertheless, the results of the mortar and concrete experiments indicate the test could be used to predict AEA adsorption and provide an estimate of the associated adjustment in AEA dosage.

Influence on Air-Void System Parameters

Mortars containing CFA required higher dosages of AEA to yield total air contents approximating those of the control mortars. An investigation was performed to identify any alteration of the air-void system that may be associated with an increased AEA dosage. Hardened mortars made with FA-G, FA-H, FA-J, and their respective control mortars were analyzed using an automated air-void analysis system. Results of this analysis are presented in Attachment C. Example data are shown in Table 4.25. Figure 4.37 presents the cumulative chord length distributions for control mortars and their respective test mortars. These results indicate slightly different air-void systems, but it is not possible to establish if this variability is statistically relevant because of the small sample size used for each condition.

Table 4.24. AEA dosages and air contents for baseline concrete mixtures.

AEA	Cementitious	AEA Dosage (oz/cwt)	Total Air Content (% vol.)
AEA-1	PC-1 Control	1.9	6.9
	PC-1 + 25% FA-A	3.5	6.4
	PC-1 + 25% FA-O	5.3	8.5
	PC-1 + 25% FA-ZN	7.7	7.1
AEA-2	PC-1 Control	1.7	5.8
	PC-1 + 25% FA-A	3.0	5.3
	PC-1 + 25% FA-O	4.2	4.9
	PC-1 + 25% FA-ZN	6.4	4.0
AEA-6	PC-1 Control	2.1	7.1
	PC-1 + 25% FA-A	3.2	6.9
	PC-1 + 25% FA-O	3.5	6.6
	PC-1 + 25% FA-ZN	4.5	5.4

Prediction of ASR Mitigation

Pyrex Mortar Bar Test (ASTM C441)

Fly ash characterization was performed using the Pyrex mortar bar expansion test (ASTM C441) currently specified in AASHTO M 295. Expansions were measured at 14 and 28 days for 25% by mass fly ash replacement of both low-alkali cement PC-1 and high-alkali cement PC-3. In Table 4.26, these expansions are expressed as (1) a percentage of expansion of low-alkali portland cement, PC-1 mortar bars (max. 100% is allowed as per AASHTO M 295), and (2) as a percentage reduction in expansion relative to high-alkali cement PC-3 mortar bars (typically reductions should be greater than 60%).

Based on these results, only fly ashes FA-H, FA-M, FA-O, and FA-Q would be considered effective in mitigating ASR expansions when used at 25% replacement. In terms of effectiveness in reducing ASR expansions, based on these data alone,

Table 4.25. Air-void parameters for control and mixtures with 25% replacement with FA-G and AEA-1.

Material	Average Chord Length (mm)	Specific Surface (mm^{-1})	Void Frequency (voids/mm)	Air Content (%)	Total Intercepts	Total Chord Length (mm)
Control	0.17	23.95	0.69	11.5	3,356	561.3
FA-G	0.16	25.48	0.79	12.4	3,778	591.3

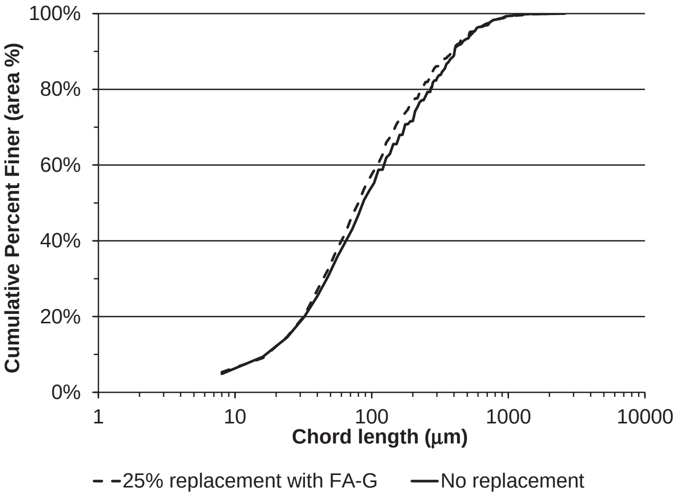

Figure 4.37. Cumulative chord length distribution for control and 25% replacement with FA-G and AEA-1.

FA-O would be the most effective, followed by FA-M, FA-Q, FA-H, FA-X, FA-ZA, FA-U, and FA-ZC.

Table 4.26. ASTM C441 Pyrex mortar bar expansion data for 25% CFA replacement.

ID (Class)	Age (Days)	Expansion (%)	Low-Alkali Cement Expansion (%)	Reduction from High-Alkali Cement Expansion (%)
FA-H (F)	14	0.179	89	63
	28	0.187	71	68
FA-M (F)	14	0.192	95	61
	28	0.221	84	62
FA-O (F)	14	0.199	99	59
	28	0.216	82	63
FA-Q (F)	14	0.159	79	67
	28	0.166	63	71
FA-U (C)	14	0.284	141	42
	28	0.312	119	46
FA-X (C)	14	0.220	109	55
	28	0.259	99	55
FA-ZA (C)	14	0.275	136	44
	28	0.302	115	48
FA-ZC (C)	14	0.350	173	28
	28	0.380	145	34

Concrete Prism Tests

With the exception of long-term outdoor exposure sites or known performance history with the same materials combination, the ASTM C1293 concrete prism test is considered to be the most reliable indicator of the effectiveness of a given level of CFA for mitigating deleterious alkali-silica reactivity. The test recommends that expansions be monitored for 2 years. The concrete prism test serves as a good reference for evaluating the effectiveness of both the current and proposed accelerated test methods. Concrete prism expansions after 12, 18, and 24 months at 38°C are given in Tables 4.27 through 4.29. In Figure 4.38, the 24-month expansions are plotted for concretes made with alkali-reactive Sudbury aggregate using PC-3 and each of the eight CFAs at a 20% and 30% replacement of cement, and for the four Class C CFAs at a 40% replacement of cement. The 12-month results indicated the four Class F CFAs (i.e., FA-H, FA-M, FA-O, and FA-Q) appeared to be effective when used at 20% replacement (i.e., the expansions were less than 0.04% at 12 months), and FA-U appeared effective when used at 30% replacement. For FA-X, a 40% replacement was required to meet the 12-month requirement, but the expansion exceeded 0.04% after 2 years. For the two Class C CFAs with the lowest sum of the oxides (i.e., FA-ZA, and FA-ZC), a 40% replacement of cement was inadequate.

After 24 months, only FA-H and FA-Q maintained expansions below 0.04% at a 20% replacement of cement. At a 30% replacement of cement, CFAs FA-O and FA-U were adequate.

Table 4.27. Twelve-month expansions (ASTM C1293 concrete prisms).

	Expansions at 12 Months (%)			
Material	0% Replacement	20% Replacement	30% Replacement	40% Replacement
PC-3 Control	0.100	–	–	–
PC-3 Control with Non-reactive Aggregate	0.030	–	–	–
FA-H	–	0.007	0.012	–
FA-M	–	0.032	0.022	–
FA-O	–	0.033	0.026	–
FA-Q	–	0.019	0.012	–
FA-U	–	0.037	0.023	0.018
FA-X	–	0.074	0.048	0.032
FA-ZA	–	0.073	0.060	0.049
FA-ZC	–	0.076	0.069	0.055

Table 4.28. Eighteen-month expansions (ASTM C1293 concrete prisms).

	Expansions at 18 Months (%)			
Material	0% Replacement	20% Replacement	30% Replacement	40% Replacement
PC-3 Control	0.116	–	–	–
PC-3 Control with Non-reactive Aggregate	0.029	–	–	–
FA-H	–	0.020	0.019	–
FA-M	–	0.049	0.038	–
FA-O	–	0.047	0.039	–
FA-Q	–	0.039	0.021	–
FA-U	–	0.049	0.031	0.021
FA-X	–	0.098	0.068	0.048
FA-ZA	–	0.082	0.069	0.057
FA-ZC	–	0.085	0.081	0.064

Table 4.29. Twenty-four-month expansions (ASTM C1293 concrete prisms).

	Expansions at 24 Months (%)			
Material	0% Replacement	20% Replacement	30% Replacement	40% Replacement
PC-3 Control	0.141	–	–	–
PC-3 Control with Non-reactive Aggregate	0.028	–	–	–
FA-H	–	0.019	0.018	–
FA-M	–	0.055	0.040	–
FA-O	–	0.053	0.033	–
FA-Q	–	0.034	0.020	–
FA-U	–	0.059	0.036	0.020
FA-X	–	0.110	0.079	0.057
FA-ZA	–	0.095	0.082	0.069
FA-ZC	–	0.100	0.097	0.076

With a replacement level of 30%, FA-M was right at the 0.04% expansion limit suggesting a 35% replacement would be adequate. At 40% replacement of cement, the low sum-of-the-oxides CFAs (FA-X, FA-ZA, and FA-ZC) exceeded 0.04% after 12, 18, and 24 months. Concrete prism expansions at 3, 6, 9, 12, 15, 18, and 24 months are provided in Attachment C.

The 24-month concrete expansions versus the sum of the oxides (i.e., $SiO_2 + Al_2O_3 + Fe_2O_3$) for each CFA, presented in Figure 4.39, show the differences between the Class F and Class C CFAs, in terms of effectiveness in mitigating deleterious ASR expansions.

Accelerated Mortar Bar Tests

The 14-day and 28-day ASTM C1567 mortar bar expansion data are shown in Tables 4.30 and 4.31 and in Figures 4.40 and 4.41; expansion data at intermediate test ages are provided in Attachment C. Although the limit used in AASHTO PP 65 is 0.10% at 14 days, the tests were continued to 28 days. Four of

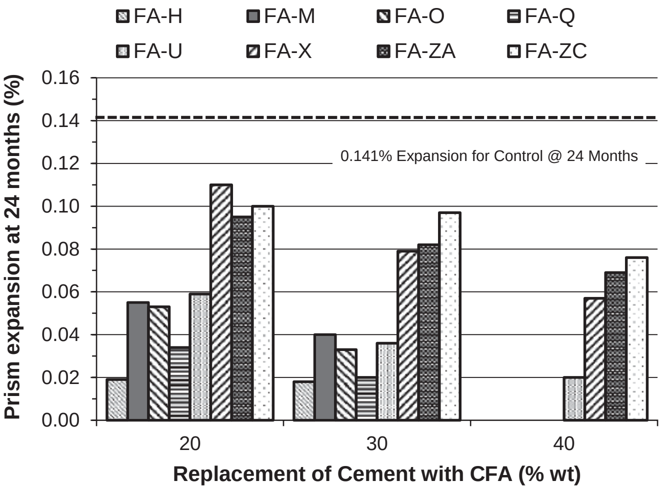

Figure 4.38. Effect of CFA replacement of cement PC-3 on 24-month concrete prism expansions.

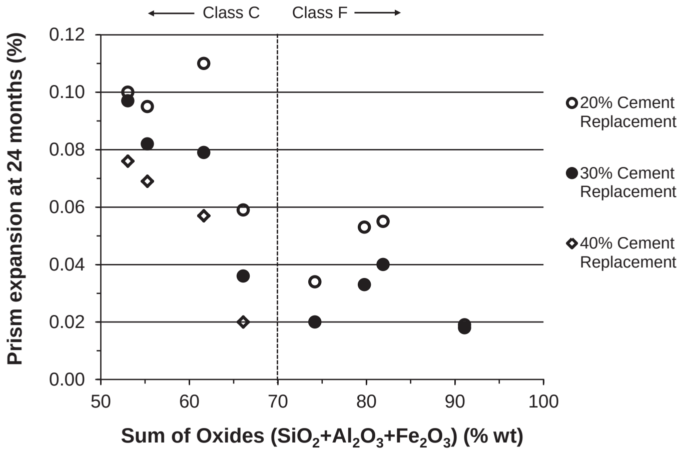

Figure 4.39. Concrete prism expansions at 24 months versus the sum of the oxides.

the mixtures (FA-O, FA-ZA, FA-ZC, and FA-X) with a 20% CFA replacement level and two mixtures (FA-ZA and FA-ZC) with a 30% replacement level showed higher expansions than the PC-3 control mixture. The 12-month expansions for all mixtures decreased as the replacement level increased above 20%, and all exhibited less expansion than the PC-3 cement control mixture at the highest replacement levels. However, the data presented in Tables 4.27 through 4.29 show that all prisms with CFA exhibited less expansion than the control with increased reduction in expansion as the replacement level increased.

For Class F CFAs, the replacement levels needed to mitigate deleterious ASR expansion based on 14-day ASTM C1567 expansions were equal or higher than those indicated by the 12-month ASTM C1293 tests and higher than indicated by the current AASHTO M 295 Pyrex mortar bar

Table 4.30. Accelerated mortar bar expansions at 14 days (ASTM C1567).

	Expansions at 14 Days (%)					
Material	0% Replace.	10% Replace.	20% Replace.	30% Replace.	40% Replace.	50% Replace.
PC-3 Control	0.23	–	–	–	–	–
PC-3 Control with Non-reactive Sand	0.05	–	–	–	–	–
FA-H	–	0.15	0.04	0.03	–	–
FA-M	–	–	0.15	0.07	0.11	–
FA-O	–	–	0.28	0.19	–	–
FA-Q	–	–	0.07	0.05	0.04	–
FA-U	–	–	0.18	0.11	0.07	–
FA-X	–	–	0.21	0.14	0.13	0.11
FA-ZA	–	–	0.26	0.23	0.19	0.11
FA-ZC	–	–	0.30	0.28	0.25	–

Table 4.31. Accelerated mortar bar expansions at 28 days (ASTM C1567).

	Expansions at 28 Days (%)					
Material	0% Replace.	10% Replace.	20% Replace.	30% Replace.	40% Replace.	50% Replace.
PC-3 Control	0.39	–	–	–	–	–
PC-3 Control with Non-reactive Sand	0.08	–	–	–	–	–
FA-H	–	0.30	0.10	0.05	–	–
FA-M	–	–	0.30	0.18	0.23	–
FA-O	–	–	0.45	0.34	–	–
FA-Q	–	–	0.20	0.10	0.06	–
FA-U	–	–	0.27	0.18	0.12	–
FA-X	–	–	0.41	0.26	0.23	0.19
FA-ZA	–	–	0.44	0.38	0.34	0.22
FA-ZC	–	–	0.46	0.42	0.34	–

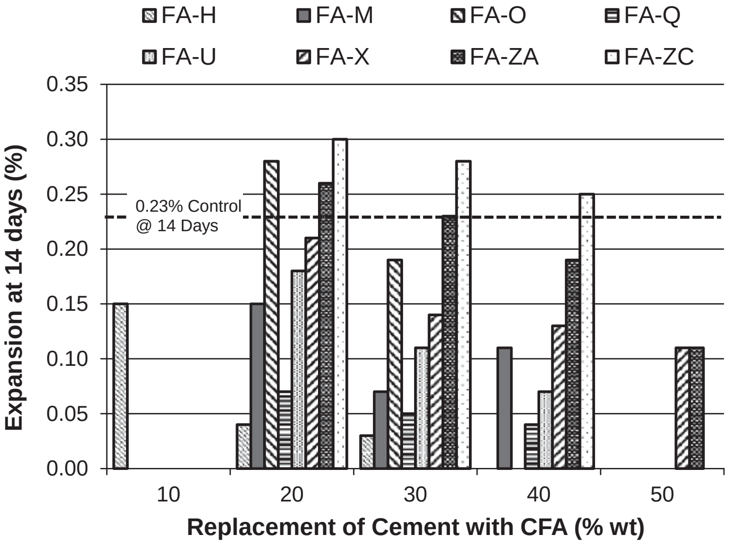

Figure 4.40. Expansions at 14 days versus cement replacement with CFA (ASTM C1567).

tests. For Class C CFAs, the levels indicated by the 14-day ASTM C1567 expansions were equal or higher than the levels indicated by the 12-month ASTM C1293 tests. If a 0.10% limit at 28 days was required by ASTM C1567, for three Class F ashes, 40% replacement of cement is not adequate. This is not in agreement with the 2-year expansions measured for the concrete prism tests (Table 4.29) at 30% replacement for Class F CFAs, suggesting an expansion limit of 0.10% at 28 days is not appropriate.

Alkali Leaching Test

The alkali leaching test was developed by Shehata and Thomas (2006) to evaluate the effectiveness of combinations of cement and CFA in binding alkalis to mitigate alkali-silica reaction. The results indicated no clear alkali release threshold for predicting concrete expansions that correlate with the ASTM C1293 expansion limit of 0.04%. Therefore, the test was not considered for further evaluation.

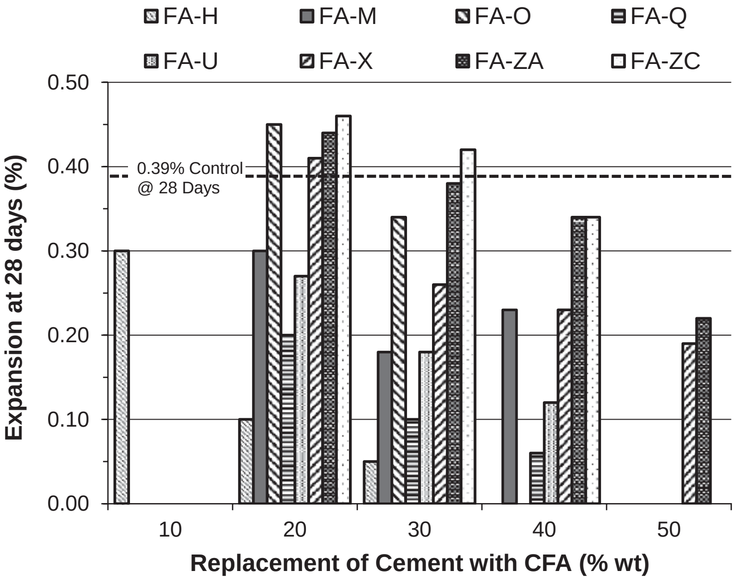

Figure 4.41. Expansions at 28 days versus cement replacement with CFA (ASTM C1567).

Table 4.32. Levels of CFA required to mitigate ASR from different tests.

	FA-H	FA-M	FA-O	FA-Q	FA-U	FA-X	FA-ZA	FA-ZC
Component	**(% wt)**							
Sum of Oxides	91.26	81.85	79.81	74.34	65.8	61.63	55.32	53.09
CaO	3.46	7.17	10.2	16.6	21.9	19.3	27.3	30.2
Na_2O_e	2.27	4.23	2.04	1.63	2.15	6.85	3.97	2.5
Test	**CFA Replacement Level (%)**							
ASTM C441	25	25	25	25	>25	>25	>25	>25
ASTM C1293								
(24 months)	20	>30	30	20	40	>40	>40	>40
ASTM C1567								
(14 days)	20	30	>30	20	40	>50	>50	>40
(28 days)	30	>40	>40	40	>40	>50	>50	>40
AASHTO PP 65								
min.% CFA*	25	30	25	25	X**	X**	X**	X**

* Based on Prevention Level Y ** Must be determined by test

The methodology and results of these test experiments are provided in Attachment C.

Comparison of ASR Test Results

Table 4.32 lists the CFA replacement levels required for meeting ASR expansion limits for various tests. When test results did not provide a definitive CFA replacement level, "greater than" (>) symbols are used. For FA-H, a 20% replacement of high-alkali cement was adequate to mitigate deleterious ASR expansion, except when a 0.10% expansion limit is used for the ASTM C1567 test at 28 days.

In Figure 4.42, 14-day mortar bar expansions (ASTM C1567) are plotted against 24-month concrete prism expansions (ASTM C1293). In AASHTO PP 65, the maximum mortar bar expansion limit for ASTM C1567 is 0.10% and for ASTM C1293 the maximum concrete prism expansion limit is 0.04% at 24 months.

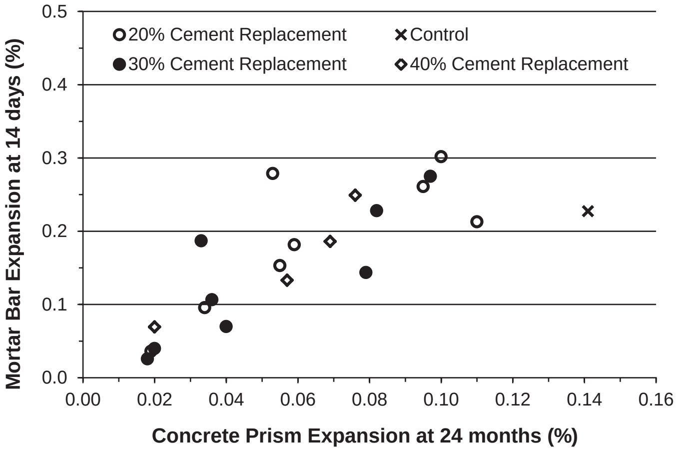

Figure 4.42. 14-day mortar bars expansions (ASTM C1567) versus 24-month concrete prism expansions (ASTM C1293).

CHAPTER 5

Conclusions and Suggested Research

Conclusions

Results of the literature review and a survey of SHAs suggested the need for improvements in tests and specifications for CFA used in highway concrete to better identify those properties affecting the concrete performance. Areas needing improvement include better characterization of (1) the strength development associated with the use of CFA, (2) the carbon fraction of CFA and its influences on air entrainment, and (3) the level of cement substitution with a specific CFA to mitigate ASR.

Improved specifications would generally require a new classification approach that better characterizes CFA performance in concrete mixtures. The purpose of classification is to group CFAs that are similar without excessive testing. The purpose of characterization is to measure and report properties that are known to affect performance, and those properties serve as a basis for the classification system. Therefore, the method used for CFA characterization may not necessarily be appropriate for use as a classification method.

For CFA characterization, 30 fly ash sources were evaluated using the test methods and specification limits stipulated in AASHTO M 295-07 and new test methods to examine the important CFA properties. As a result, refinements to existing CFA characterization protocols were proposed, and changes to AASHTO M 295-11 were made to provide better prediction of CFA performance within the framework of the existing classification method.

Changes to Chemical Requirements

Chemical Classification

The primary distinction between Class F and Class C CFA is the bulk composition based on the sum of the oxides (i.e., $\%SiO_2 + \%Al_2O_3 + \%Fe_2O_3$). However, this classification omits consideration of calcium content. This research has shown a clear, linear relationship between the sum of the oxides and the calcium content; therefore, specifying either characteristic would provide the same result.

Although there was no unique relationship between calcium oxide content and CFA performance to serve as a basis for classification, above a threshold of approximately 15%, there was evidence of a decreasing effectiveness for mitigating sulfate attack or ASR (Dhole et al., 2011; Thomas, 2011). Therefore, determining the calcium content is important and is proposed for inclusion in Table 1 of AASHTO M 295. Reporting the calcium oxide content and the magnesium oxide, sodium oxide, potassium oxide, and the equivalent alkali (Na_2O_e) content is also proposed. It should be noted that AASHTO PP 65 requires the CaO and Na_2O_e values for determining strategies for ASR mitigation.

Effects on Air Entrainment

To assess the effect of a CFA on air entrainment, AASHTO M 295 calls only for determining the LOI content of the ash. However, this single measure has been shown to not be sufficient. In this research, an experimental investigation was conducted to develop new tests for predicting the AEA demand of CFA. This investigation included evaluation of the foam index test and development of two new tests: the CFA iodine number and direct adsorption isotherm tests.

After review and conduct of a wide range of foam index tests, a modified version of the test method by Harris et al. (2008a) was proposed as a standard test. The modifications included using a range of standard solution concentrations to determine the solution that achieves a stable foam in a consistent time (15 ± 3 min) for that fly ash. The solution strength is determined by iteration and a procedure is provided in Attachment B. The proposed test time allows for the CFA to achieve a consistent degree of contact with the AEA solution, although not necessarily long enough to achieve equilibrium. The modified Harris test specifies incremental addition of AEA to minimize the error associated with adding AEA to the slurry and requires use of a mechanical agitator to minimize operator-induced variability.

Overall, the foam index test is suitable for assessing CFA and AEA interactions, but it is not necessarily suitable for assessing the influence of CFA on air entrainment. Even with the proposed improvements, the test has a high level of subjectivity and variability. To enhance applicability, there was a need for developing a standard approach for conducting the test.

The CFA iodine number and the direct adsorption isotherm tests are recommended to be included in AASHTO M 295 as a Supplementary Optional Chemical Requirement for assessing the adsorption potential of a specific CFA source. The research has shown that CFA sources with a CFA iodine number ≤ 0.1 mg iodine/gram CFA have little impact on air entrainment, and a CFA with an iodine number > 0.1 mg iodine/gram CFA may have some effect on air entrainment. However, the CFA iodine number characterizes only the CFA, and it is necessary to evaluate both the CFA and AEA as a system. Therefore, establishing an upper threshold for the CFA iodine number is not possible without defining the AEA to be used. From a classification perspective, it is recommended to retain the LOI measure as a means of limiting the maximum carbon content, rather than establishing a maximum CFA iodine number. Instead, the CFA iodine number and direct adsorption isotherm test can be used as a means for identifying those CFA sources that have a potential to adversely influence air entrainment. The CFA iodine number is recommended for use as a screening test. If the test results in a value > 0.1 mg iodine/gram CFA, a direct adsorption isotherm is required with a specified AEA and the capacity determined for the CFA-AEA combination is reported to provide the user with a quantitative measure of the effect of the CFA on air entrainment.

Another consideration is the use of powdered activated carbon (PAC) for pollution control in power plants, which significantly increases the adsorption capacity of the CFA with potentially only a small change in the LOI. PAC has an adsorption potential much higher than carbon in CFA resulting from combustion. Both the CFA iodine number and direct adsorption isotherm tests are extremely sensitive to the inclusion of PAC and can quantify its effect on air entrainment.

This research has shown the CFA iodine number and the direct adsorption isotherm test can be used together by performing both tests on a suite of fly ash sources that covers the expected range of carbon content. The direct adsorption isotherm test is performed using the AEA of interest. When the CFA iodine number is plotted versus the direct adsorption isotherm test, iodine capacity can be converted directly to AEA capacity. The user then only needs to measure the iodine number for any new CFA source being used with the same AEA. To implement this approach, the CFA iodine number versus direct adsorption isotherm relationships for the AEAs will need to be determined. In this case, the specification would only require reporting the CFA iodine number. The approach of correlating the CFA iodine number and the direct adsorption isotherm test depends on the consistency of the AEA adsorption characteristics. If the adsorption capacity of an AEA varies with production, the correlation would vary and would need to be repeated. The CFA iodine number test uses standard chemicals making it less subjective. An alternative application of the direct adsorption isotherm test would be to evaluate specific AEAs with one CFA source to allow users to select the AEA that performs best with this CFA source. Given that a concrete producer tends to use the same source of CFA, but numerous AEAs are available, the approach of matching materials would have practical advantages.

Available Alkali Limit

The available alkali test currently specified in AASHTO M 295 takes over 1 month to complete, and its precision is questionable. A preferable alternative is to base the classification on the determined potassium oxide and sodium oxide contents (i.e., total alkali). ASTM C441, ASTM C1567, and ASTM C1293 failed to provide acceptable correlations with available alkali test results. Given the limitations of the available alkali test, and total alkali limits in AASHTO PP 65 that greatly exceed the current available alkali limits, the requirement for the available alkali limit would be better replaced with the total alkali contents to establish required levels of ASR mitigation in AASHTO PP 65.

Changes to Physical Requirements

Strength Activity Testing

The current strength activity index (SAI) has a minimum strength requirement that can be met by inert materials (i.e., finely ground quartz). This research showed that increasing the 7-day limit from 75% to 85% would be appropriate for rejecting inert material.

An alternative to the SAI test method is the pozzolanic activity index (PAI) using 35% by mass replacement of cement with CFA, together with accelerated curing. This test is similar to ASTM C1240, *Standard Specification for Silica Fume Used in Cementitious Mixtures,* where mortar cubes are moist cured for 7 days at 65°C. However, developing an accelerated PAI test method would need considerable refinement and an interlaboratory study to provide a 7-day test criterion for Class F fly ashes (the old AASHTO M 295 PAI test includes only a 28-day criterion).

The Keil hydraulic index (KHI) was investigated as a potential replacement for the current SAI test. The results of that analysis showed that KHI values are not significantly different from those obtained by the SAI test, but the test better defines the effect of a CFA on strength contribution at different ages and replacement levels. Also, specimens prepared using inert fillers did not pass the KHI test using existing SAI limits. The KHI test showed an influence of the type of portland cement used (a similar influence was seen in the SAI test). This research also indicated the type of inert filler used had negligible effect on 28-day strengths. Additional refinement and an inter-laboratory study are required to provide appropriate test criteria for the KHI test.

The KHI and PAI tests require further development. Therefore, the SAI test should remain part of the AASHTO M 295 specification. To address the issue of inert fillers meeting the SAI test requirement, the minimum SAI needs to be raised to 85% at 7, 28, or 56 days of age. The current AASHTO specification requires a CFA to meet the strength index requirement at 7 or 28 days, or at 56 days only if specified by the purchaser. This research showed that Class F ashes not meeting the 7-day limit of 85% would meet the 85% limit at 28 or 56 days.

ASR Mitigation

The AASHTO M 295 standard test for ASR mitigation uses Pyrex glass as a synthetic alkali-silica reactive aggregate, which is readily available and can be used to compare the performance of CFAs. However, the ability of a CFA to mitigate deleterious ASR expansions is influenced by the type of reactive aggregate used in concrete. Also, the performance criterion for the test method is vaguely stated and may not provide a reliable level of performance. ASTM C1567 uses the proposed job aggregate to determine an effective level of cement replacement using a particular CFA. Both tests can be completed in about 2 weeks after preparing the mortar bars. Because AASHTO PP 65 makes use of the ASTM C1567 test, it is recommended the test be incorporated into AASHTO M 295 with a requirement for a maximum expansion limit of 0.10% after 14 days of exposure in NaOH solution.

The research also indicated that the expansion limit of 0.10% after 28 days for evaluating ASTM C1567 results was not obtained by three of the four Class F ashes with 40% replacement of cement, and the results differed from those obtained from the 2-year concrete prism tests (ASTM C1293) and the performance of Class F ash with aggregates of similar type and level of reactivity. These findings indicate that this evaluation criterion is inappropriate.

The ASTM C1293 concrete prism test allows testing of both the coarse and fine aggregates but requires an excessive time period to complete (2 years is recommended in ASTM C1293 and AASHTO PP 65).

Changes to Testing Requirements

Moisture content and LOI tests are currently limited to a sample mass of 1 g. The small sample mass can affect the precision of the results, particularly for low values. Increasing the sample mass would eliminate this concern. Increased sample mass can be accomplished by modifying the moisture content and LOI test methods in ASTM C311 by removing the reference to the procedure in ASTM C114, which involves a 1 g sample requirement and a reheat requirement (i.e., constant mass requirement). Laboratories may select the length of the ignition time and sample mass using reference materials to document both the precision and bias of the procedure.

This research showed some inconsistency in sulfur (SO_3) determinations caused by a loss of SO_3 in the LOI determination. Therefore, it is proposed that the potential for SO_3 loss during the LOI procedure be noted in AASHTO M 295.

Suggested Research

The following suggestions for future research are made to improve specifications and test methods for CFA:

1. Develop a precision statement for the foam index, CFA iodine number, and direct adsorption isotherm tests
2. Establish the relationship between the CFA iodine number and the direct adsorption isotherm tests for a range of AEAs
3. Develop a modified PAI test method using 35% CFA by mass replacement of cement and accelerated curing (e.g., 55°C) with consideration for using a fixed *w/cm*
4. Establish appropriate specification limits for the mortar air content test and the shrinkage test (with the CFA being treated as a cement replacement)
5. Develop a water-soluble alkali test for CFA, precision information, and specification limits.

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Acronyms

AEA	Air entraining admixture or agent
ASR	Alkali-silica reactivity
AASHTO	American Association of State Highway Officials
CCRL	Cement and Concrete Reference Laboratory
COD	Chemical oxygen demand
CFA	Coal fly ash
DTA	Differential thermal analysis
FHWA	Federal Highway Administration
ITZ	Interfacial transition zone
KHI	Keil hydraulic index
LOI	Loss on ignition
NCHRP	National Cooperative Highway Research Program
NIST	National Institute of Standards and Technology
PCC	Portland cement concrete
PAC	Powdered activated carbon
PAI	Pozzolanic Activity Index
QXRD	Quantitative x-ray diffraction
RIR	Relative intensity ratio
SHA	State highway agencies
SAI	Strength Activity Index
SCM	Supplementary cementitious materials
TGA	Thermal gravimetric analysis
TMA	Thermomechanical analysis
w/cm	Water-cementitious material ratio
XRD	X-ray diffraction
XRF	X-ray fluorescence

ATTACHMENT A

Summary of Proposed Changes to AASHTO M 295-11, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*

These proposed changes to AASHTO M 295, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete,* are the suggestions of the NCHRP Project 18-13 research team. These changes have not been approved by NCHRP or any AASHTO committee nor formally accepted for the AASHTO specifications.

In this summary, the proposed deletions are indicated by strikethrough text and proposed insertions indicated by underlined text.

Specification Change	**Commentary**
Section 2.1 Add references for the new coal fly ash iodine number and direct adsorption isotherm tests.	Both are new test methods added to the specification.
Section 2.2 Add references for ASTM C1567.	ASTM C1567 added to replace ASTM C441.
Section 4.3 Note 3. Note 3 - Class F fly ash is typically produced from burning anthracite or bituminous coal, but may also be produced from subbituminous coal and from lignite. Class C fly ash is typically produced from burning lignite or subbituminous coal, and may also be produced by anthracite or bituminous coal. ~~Class C fly ashes contain total calcium contents, expressed as calcium oxide (CaO), higher than 10 percent.~~ Class C fly ashes typically have total calcium contents, expressed as calcium oxide (CaO), that are higher than Class F fly ashes.	This change is proposed to provide clarity to specifiers. It is confusing to have a numerical, quantitaive limit for CaO content in a note when CaO is not specified in Table 1. Also, this change is proposed to keep AASHTO M 295 consistent with ASTM C618. ASTM has recently approved the same change.
Section 5.1 5.1 The purchaser shall specify any supplementary optional ~~chemical and physical~~ requirements.	This change is proposed for clarity. The reference to supplementary optional chemical and physical requirements is redundant given the only supplementary optional requirements are chemical and physical supplementary optional requirements.
Table 1 – Chemical Requirements Modify Table 1 as shown below.	Classify the ash using the sum of the oxides reported to the nearest whole number to reflect the precision of the actual chemical determination. Add a maximum sum of the oxides value to Class C ash to eliminate Class Fashes also qualifying as Class C ashes. Report CaO, MgO, Na_2O, K_2O, and equivalent alkali to provide specifiers more information about the coal fly ash and also to provide information necessary to apply AASHTO PP 65, *Standard Practice for Determining the Reactivity of Concrete Aggregates and Selecting Appropriate Measures for Preventing Deleterious Expansion in New Concrete Construction*.

Table 1. Chemical requirements.

	Coal Fly Ash and Raw or Calcined Natural Pozzolan Class		
	N	F	C
Silicon dioxide (SiO_2) plus aluminum oxide ($A1_2O_3$) plus iron oxide (Fe_2O_3), percent	70~~.0~~ min	70~~.0~~ min	50~~.0~~ min, less than 70
Sulfur trioxide (SO_3), max percent	4.0	5.0	5.0
Moisture content, max percent	3.0	3.0	3.0
Loss on ignition, max percent	5.0	5.0	5.0
Calcium oxide (CaO), percent	no limit – report only	no limit – report only	no limit – report only
Magnesium oxide (MgO), percent	no limit – report only	no limit – report only	no limit – report only
Sodium oxide (Na_2O), percent	no limit – report only	no limit – report only	no limit – report only
Potassium oxide (K_2O), percent	no limit – report only	no limit – report only	no limit – report only
Equivalent alkali (Na_2O_e)[a], percent	no limit – report only	no limit – report only	no limit – report only

[a] $Na_2O_e = Na_2O + (0.658 \times K_2O)$

Specification Change	**Commentary**
Section 6.2 ~~6.2 Other oxides commonly reported for fly ash include CaO, MgO, Na_2O and K_2O.~~	Redundant with changes to Table 1.
Table 2 - Supplementary Optional Chemical Requirements Modify Table 2 as shown below.	Delete available alkali limits due to limitations and poor precision of the test. Replace this requirement with reporting total alkalis in Table 1 to be consistent with AASHTO PP 65. Add determination and reporting of the coal fly ash iodine number (AASHTO T XXX) and, if necessary, determine and report the Air-Entraining Admixture Adsorption by Coal Fly Ash (AASHTO T YYY). These two tests provide an approach to quantifying the adsorption of air-entraining admixtures by coal fly ash.

Table 2. Supplementary optional chemical requirements.

	Coal Fly Ash and Raw or Calcined Natural Pozzolan Class		
	N	F	C
~~Available alkalies, or equivalent, as Na_2O, max percent[a]~~	~~1.5~~	~~1.5~~	~~1.5~~
Coal fly ash iodine number (AASHTO T XXX)[a]	not applicable	report coal fly ash iodine number	

~~[a] Applicable only when specifically required by the purchaser for mineral admixture to be used in concrete containing reactive aggregate and cement to meet a limitation on content of alkalies~~

[a] If the reported value for the coal fly ash iodine number (AASHTO T XXX) is greater than 0.10 mg iodine/gram coal fly ash, then perform AASHTO T YYY (Determination of Air-Entraining Admixture Adsorption by Coal Fly Ash) using a single air-entraining agent specified by the ash purchaser, and report both the coal fly ash iodine number and the information specified in the reporting section of AASHTO T YYY.

Specification	Commentary
Table 3 - Physical Requirements Modify Table 3 as shown below.	Increase the 7- and 28-day limit for the strength activity index (SAI) to 85 to protect inert (non-pozzolanic) materials from passing the test. Allow for qualification for SAI at 28 and 56 days to allow Class F ashes with low early strength gain to qualify. Editorial changes to Note B to eliminate references to accelerated tests, "expected" contribution to strength, and a redundant reference to testing with portland cement. By definition, the SAI test is performed with portland cement.

Table 3. Physical requirements.

	Coal Fly Ash and Raw or Calcined Natural Pozzolan Class		
	N	F	C
Fineness:			
Amount retained when wet-sieved on 45 μm (No. 325) sieve, max percent[a]	34	34	34
Strength activity index:[b]			
With portland cement, at 7, 28, or 56 days, min percent of control	75	~~75~~ 85~~[e]~~ [d]	~~75~~ 85~~[e]~~ [d]
~~With portland cement, at 28 or 56[e] days, min percent of control~~	~~75~~	~~75[e]~~	~~75[e]~~
Water requirement, max percent of control	115	105	105
Soundness:~~[d]~~ [c]			
Autoclave expansion or contraction, max percent	0.8	0.8	0.8
Uniformity requirements:			
The density and fineness of individual samples shall not vary from the average established by the 10 preceding tests, or by all preceding tests if the number is less than 10, by more than:			
Density, max variation from average, percent	5	5	5
Percent retained on 45 μm (No. 325) sieve, max variation, percentage points from average	5	5	5

[a] Care should be taken to avoid the retaining of agglomerations of extremely fine material.

[b] The strength activity index with portland cement is not to be considered a measure of the compressive strength of concrete containing the coal fly ash and raw or calcined natural pozzolan. ~~The strength activity index with portland cement is determined by an accelerated test, and is intended to evaluate the contribution to be expected from the coal fly ash and raw or calcined natural pozzolan to the longer strength development of concrete.~~ The mass of coal fly ash and raw or calcined natural pozzolan specified for the test to determine the strength activity index ~~with portland cement~~ is not considered to be the proportion recommended for the concrete to be used in the work. The optimum amount of coal fly ash and raw or calcined natural pozzolan for any specific project is determined by the required properties of the concrete and other constituents of the concrete and should be established by testing. Strength activity index with portland cement is a measure of reactivity with a given cement and is subject to variation depending on the source of both the coal fly ash and raw or calcined natural pozzolan and the cement.

~~[e] Only applicable when testing at 56 days is specified.~~

~~[d]~~ [c] If the coal fly ash and raw or calcined natural pozzolan will constitute more than 20 percent by mass of the cementitious material in the project mix design, the test specimens for autoclave expansion shall contain that anticipated percentage. Excessive autoclave expansion is highly significant in cases where water to coal fly ash and raw or calcined natural pozzolan and cement ratios are low, for example, in block or shotcrete mixes.

~~[e]~~ [d] Meeting the 7-day, 28-day, or 56-day (if specified) strength activity index will indicate specification compliance.

Specification	Commentary
Table 4 - Supplementary Optional Physical Requirements Modify Table 4 as shown below.	Modifications involve elimination of ASTM C441 and insertion of ASTM C1567 for determining effectiveness in controlling alkali-silica reaction. The acceptance limits of 0.10 max percent are consistent with AASHTO PP 65. Note B eliminated as it referred specifically to ASTM C441. Reletter remaining notes accordingly.

Table 4. Supplementary optional physical requirements.

	Coal Fly Ash and Raw or Calcined Natural Pozzolan Class		
	N	F	C
Increase of drying shrinkage of mortar bars at 28 days, max difference in percent over control[a]	0.03	0.03	0.03
Uniformity requirements:			
In addition, when air-entrained concrete is specified, the quantity of air-entraining agent required to produce an air content of 18.0 vol percent of mortar shall not vary from the average established by the 10 preceding tests or by all preceding tests if less than 10, by more than, percent	20	20	20
Effectiveness in controlling alkali-silica reaction (as per ASTM C1567):			
Expansion of test mixture ~~as percentage of low-alkali cement control,~~ at 14 days, max percent	~~100~~ 0.10	~~100~~ 0.10	~~100~~ 0.10
Effectiveness in contributing to sulfate resistance: [b]			
Procedure A:			
Expansion of test mixture:			
For moderate sulfate exposure after 6 months of exposure, max percent	0.10	0.10	0.10
For high sulfate exposure after 6 months of exposure, max percent	0.05	0.05	0.05
Procedure B:			
Expansion of test mixture as a percentage of sulfate resistance cement control after at least 6 months of exposure, max percent	100	100	100

[a] Determination of compliance or noncompliance with the requirement relating to increase in drying shrinkage will be made only at the request of the owner.

~~[b]~~ ~~Coal fly ash and raw or calcined natural pozzolans meeting this requirement are considered as effective in controlling alkali-aggregate reactions as the use of the low-alkali control cement used in the evaluation. However, the coal fly ash and raw or calcined natural pozzolan shall be considered effective only when the coal fly ash and raw or calcined natural pozzolan are used at percentages by mass of the total cementitious material equal to or exceeding that used in the tests and when the alkali content of the cement to be used with the coal fly ash and raw or calcined natural pozzolan does not exceed that used in the tests by more than 0.05 percent. See Appendix X1, ASTM C 311.~~

[b] Fly ash or natural pozzolan shall be considered effective only when the fly ash or natural pozzolan is used at percentages, by mass, of the total cementitious material within 2 percent of those that are successful in the test mixtures or between 2 percentages that are successful, and when the C_3A content of the project cement is less than or equal to that which was used in the test mixtures. See Appendix X2 of ASTM C311.

Note: These optional requirements apply only when specifically requested.

ATTACHMENT B

Draft Proposed New Test Methods

These proposed test methods are the suggestions of the NCHRP Project 18-13 research team. These test methods have not been approved by NCHRP or any AASHTO committee nor formally accepted for the AASHTO Specifications.

Contents

Proposed Method of Test for

Determination of the Foam Index of a Coal Fly Ash and Portland Cement Slurry

1. SCOPE

1.1. This test method is for the determination of the foam index of a mixture of coal fly ash, portland cement, water, and an air-entraining admixture.

1.2. The foam index can be used as a relative measure of the effect of a specific coal fly ash on the process of air entrainment in concrete batched using the same fly ash, portland cement, and air-entraining agent as used in the test procedure.

1.3. The values stated in SI units are to be regarded as the standard.

1.4. *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations to use.*

Warning—Fresh hydraulic cementitious mixtures are caustic and may cause chemical burns to skin and tissue upon prolonged exposure (Note 1).

Note 1—The safety precautions given in the Manual of Aggregate and Concrete Testing, located in the related section of Volume 04.02 of the Annual Book of ASTM Standards, are recommended.

1.5. The text of these standard reference notes provides explanatory material. These notes (excluding those in tables and figures) shall not be considered as requirements of the standard.

2. REFERENCED DOCUMENTS

2.1. *ASTM Standards*:

- C125, *Standard Terminology Relating to Concrete and Concrete Aggregates*
- C311, *Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete*

3. TERMINOLOGY

3.1. *Definitions*:

3.1.1. The terms used in this specification are defined in ASTM C125.

4. SUMMARY OF TEST METHOD

4.1. The foam index test is used to estimate the effect of a specific coal fly ash on the air entrainment of concrete prepared with a specific portland cement and air-entraining admixture combination. The test is performed by visually noting the stability of the foam produced when the coal fly ash, portland cement and air-entraining admixture are combined with water and agitated. The test is designed to achieve a foam index value in 15 ± 3 min when conducted using an air-entraining admixture solution strength appropriate for the coal fly ash being tested.

5. SIGNIFICANCE AND USE

5.1. The test provides an indication of possible changes in the amount of air-entraining admixture required when using the same materials combination in concrete.

5.2. The foam index is not an absolute measure of air-entraining admixture dosage for a concrete mixture.

5.3. The test result can be expressed in a number of different ways, depending upon the need of the users, as presented in Section 9.

6. APPARATUS

6.1. *Pipette*—capable of delivering a drop volume of 0.02 mL per drop.

6.1.1. Pipette should be calibrated prior to use in accordance with standard laboratory procedures.

6.2. *250 mL Wide-Mouth Nalgene®-Type Container with a Tight-Fitting Screw Top Lid.*

6.3. *Wrist-Action-Type Laboratory Shaker*—capable of holding a 250 mL wide-mouth Nalgene-type container.

6.3.1. Wrist-action-type laboratory shaker should be adjustable in sample displacement and have timer control capable of producing a 10 s and 30 s shake cycle. An example is shown in Figure 1.

Figure 1. Example of a wrist-action-type laboratory shaker.

7. MATERIALS

7.1. *Coal Fly Ash*—a grab sample, regular sample, or composite sample as described in C311, Sections 6.1–6.3.

7.2. *Portland Cement*—a 2 to 4 kg sample of the portland cement that is to be used, along with the coal fly ash, in the final concrete mixture.

7.3. *Distilled Water*—an adequate supply of distilled water.

7.4. *Air-Entraining Admixture*—an adequate supply of the air-entraining admixture to be used, along with the coal fly ash, in the final concrete mixture.

7.4.1. The air-entraining admixture should be prepared as standard aqueous solutions to be used for testing. The concentration of the standard solutions can vary depending upon the coal fly ash and air-entraining admixture being tested. Recommended solution strengths are 2%, 6%, 10%, and 15% air-entraining admixture by volume. Solutions of any known concentration can be used.

7.4.2. To ensure accuracy in mixing standard solutions, a minimum of 1 L of solution should be prepared.

7.4.3. Consult the air-entraining admixture manufacturer's recommendations regarding the shelf life of the prepared solutions.

8. PROCEDURE

8.1. *Determine Blank Sample Air-Entraining Admixture Requirements (Optional)*

8.1.1. This part of the procedure establishes the air-entraining admixture needed to achieve a stable foam with cement only. Depending upon how the results of the foam index test are to be presented and used, this portion may be optional.

8.1.1.1 Determine the initial solution concentration to use for the test. For cement, the lowest concentration solution should suffice.

8.1.1.2 In a 250 mL wide-mouth Nalgene-type container with a tight-fitting cap, combine 25 mL distilled water and 10 g of portland cement and tightly seal the container.

8.1.1.3 Secure container in the wrist-action shaker and agitate the container for 30 s, displacing it vertically approximately 20 cm.

8.1.1.4 Open the cap on the container.

8.1.1.5 With the container still in the wrist-action shaker, pipette a single drop (0.02 mL) of air-entraining admixture solution and tightly reseal the container.

8.1.1.6 Agitate the container with the wrist-action shaker for 10 s, displacing it vertically approximately 20 cm.

8.1.1.7 With the container still in the wrist-action shaker, open the cap, leaving the container undisturbed, and observe the contents at the air-slurry interface for foam.

8.1.1.8 If no foam is present or the foam is stable for less than 15 s, repeat Steps 8.1.1.4–8.1.1.7 until a stable foam remains for 15 s.

Note 2—*A stable foam is defined as a continuous foam cover at the air/liquid interface.*

8.1.1.9 If the stable foam is achieved within a total test time of 12 to 18 min, record the total number of drops of air-entraining admixture solution added to achieve a stable foam ($N_{D\ cement}$), the solution concentration of the air-entraining admixture solution used ($C_{S\ cement}$), and the total test time (t_{cement}).

8.1.1.10 If the stable foam is achieved outside of 12 to 18 min, adjust the solution concentration as described in Figure 2 and proceed from Step 8.1.1.2.

8.2. *Determine Combined Portland Cement & Coal Fly Ash Air-Entraining Admixture Requirements*

8.2.1. This part of the procedure establishes the air-entraining admixture needed to achieve a stable foam with portland cement and coal fly ash combined.

8.2.1.1 Determine the initial solution concentration to use for the test. For blends of cement and coal fly ash, the choice will be based upon experience or available information [e.g., known loss on ignition (LOI)].

8.2.1.2 In a 250 mL wide-mouth Nalgene-type container with a tight-fitting cap, combine 25 mL of distilled water, 8 g of portland cement, and 2 g of coal fly ash and tightly seal the container.

8.2.1.3 Secure the container in the wrist-action shaker and agitate the container for 30 s, displacing it vertically approximately 20 cm.

8.2.1.4 Open the cap on the container.

8.2.1.5 With the container still in the wrist-action shaker, pipette a single drop (0.02 mL) of air-entraining admixture solution and tightly reseal the container.

8.2.1.6 Agitate the container with the wrist-action shaker for 10 s, displacing it vertically approximately 20 cm.

8.2.1.7 With the container still in the wrist-action shaker, open the cap, leaving the container undisturbed, and observe the contents at the air-slurry interface for foam.

8.2.1.8 If no foam is present or the foam is stable for less than 15 s, repeat Steps 8.2.1.4–8.2.1.7 until a stable foam remains for 15 s.

8.2.1.9 If the stable foam is achieved within a total test time of 12 to 18 min, record the total number of drops of air-entraining admixture solution added to achieve a stable foam ($N_{D\ ash}$), the solution concentration of the air-entraining admixture solution used ($C_{S\ ash}$), and the total test time (t_{ash}).

8.2.1.10 If the stable foam is achieved outside of 12 to 18 min, adjust the solution concentration as described in Figure 2 and proceed from Step 8.2.1.2.

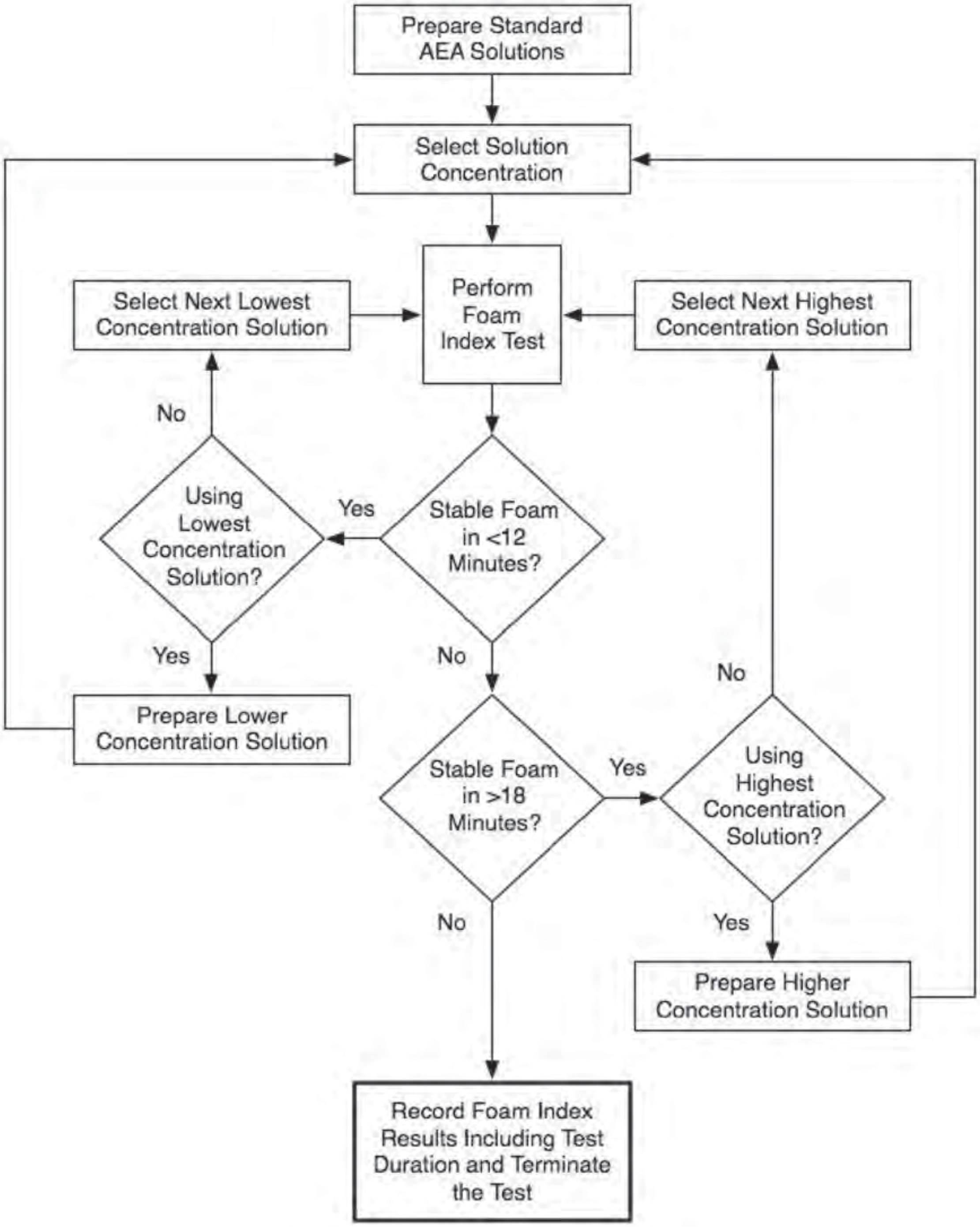

Figure 2. Protocol for conducting the foam index test and establishing the optimum AEA solution concentration to achieve an endpoint in 15 ± 3 min.

9. CALCULATION

9.1. The results of the foam index test can be expressed many different ways. Each of these may have application depending upon the purposes of the test.

9.1.1. Calculations are based on 10 g of cementitious material for all tests conducted.

9.1.2. Data collected will consist of:

$N_{\mathrm{D\ cement}}$ = number of drops of air-entraining admixture solution added to cement-only sample

$C_{\mathrm{S\ cement}}$ = concentration of air-entraining admixture solution added to cement-only sample

$N_{\mathrm{D\ ash}}$ = number of drops of air-entraining admixture solution added to cement/coal fly ash sample

$C_{\mathrm{S\ ash}}$ = concentration of air-entraining admixture solution added to cement/coal fly ash sample

9.2. $\mathit{Foam\ Index}_{\mathrm{cement}} = N_{\mathrm{D\ cement}} \bullet 0.02$

9.3. $\mathit{Foam\ Index}_{\mathrm{ash}} = N_{\mathrm{D\ ash}} \bullet 0.02$

9.4. $\mathit{Absolute\ Volume}_{\mathrm{cement}} = N_{\mathrm{D\ cement}} \bullet 0.02 \bullet C_{\mathrm{S\ cement}}$

9.5. $\mathit{Absolute\ Volume}_{\mathrm{ash}} = N_{\mathrm{D\ ash}} \bullet 0.02 \bullet C_{\mathrm{S\ ash}}$

9.6. $\mathit{Specific\ Foam\ Index}_{\mathrm{cement}} = \mathit{Absolute\ Volume}_{\mathrm{cement}} \bullet 10{,}000$

9.7. $\mathit{Specific\ Foam\ Index}_{\mathrm{ash}} = \mathit{Absolute\ Volume}_{\mathrm{ash}} \bullet 10{,}000$

9.8. $\mathit{Relative\ Foam\ Index} = \left[(\mathit{Absolute\ Volume}_{\mathrm{ash}}) / (\mathit{Absolute\ Volume}_{\mathrm{cement}})\right] * 100$

Where:

Foam Index = volume of diluted air-entraining admixture solution added in the test, mL

Absolute Volume = volume of undiluted air-entraining admixture solution added in the test, mL

Specific Foam Index = undiluted air-entraining admixture per 100 kg cementitious material, mL

Relative Foam Index = ratio of air-entraining admixture needed for cementitious mixture containing coal fly ash and air-entraining admixture required for cement-only mixture, expressed as a percentage of air-entraining admixture required for cement-only mixture

10. REPORT

10.1. Report the following information

- Time and date of test
- Fly ash source tested
- Portland cement tested
- Air-entraining admixture tested
- Solution strength (both $C_{\mathrm{S\ cement}}$ and $C_{\mathrm{S\ ash}}$ as applicable)
- Total test time (both t_{cement} and t_{ash} as applicable)
- Results of equations in Steps 9.2–9.8 (as applicable)

11. PRECISION AND BIAS

11.1. *Precision*—A precision statement for this test has not yet been established.

11.2. *Bias*—There is no accepted standard sample that can be used to establish bias.

12. KEYWORDS

12.1. Coal fly ash; air-entraining admixture; foam index.

Proposed Modifications to ASTM D4607 for Determining the Iodine Number for Coal Fly Ash

The following are proposed modifications to ASTM D4607, *Standard Test Method for Determination of Iodine Number of Activated Carbon*, necessary for the determination of the iodine number for coal fly ash.

It is proposed to replace several sections in ASTM D4607 with new sections; the proposed new sections are shown below. In addition, an unnumbered new section titled Materials is proposed for insertion after Section 5 Apparatus. Subsequent sections would need to be renumbered.

3. Summary of Test Method

3.1. This test method is based upon a four-point adsorption isotherm (see Practices D3860). A standard iodine solution is treated with four different weights of coal fly ash under specified conditions. The fly ash treated solutions are filtered to separate the fly ash from the treated iodine solution (filtrate). Iodine remaining in the filtrate is measured by titration. The amount of iodine removed per gram of fly ash is determined for each fly ash dosage and the resulting data used to plot an adsorption isotherm. The amount of iodine adsorbed (in milligrams) per gram of fly ash at a residual iodine concentration of 0.01 N is reported as the coal fly ash iodine number.

3.2. Iodine concentration in the standard solution affects the capacity of carbon for iodine adsorption. Therefore, the normality of the standard iodine solution must be maintained at a constant value (0.025 ± 0.001 N) for all iodine number measurements.

3.3. The apparatus required consists of various laboratory glassware used to prepare solutions and contact coal fly ash with the standard iodine solution. Filtration and titration equipment are also required.

4. Significance and Use

4.1. Coal fly ash is composed of inorganic and organic phases with the organic phases occurring as unburned carbon resulting from the coal combustion process. Carbon may also be present when used for flue gas treatment to meet emission criteria. The carbon is assumed to be the sole adsorbent of iodine.

4.2. The iodine number is a relative indicator of porosity in activated carbon. It does not necessarily provide a measure of the carbon’s ability to absorb other species. Iodine number may be used as an approximation of surface area for some types of activated carbons (see Test Method C819). However, it must be realized that any relationship between surface area and iodine number cannot be generalized. It varies with many factors relating to the source of the carbon and the conditions under which it is produced in the combustion process.

4.3. The presence of adsorbed volatiles, sulfur, and water extractables may affect the measured iodine number of an activated carbon in coal fly ash. This procedure includes a pre-treatment step to remove sulfur known to exist in coal fly ash.

5. Apparatus

5.1. *Analytical Balance*—accuracy ± 0.0001 g.

5.2. *Buret*—25 mL capacity precision buret with stand.

5.3. *Flasks*—Erlenmeyer 250 mL capacity with a ground glass stopper or rubber stopper.

5.4. *Flask*—Erlenmeyer wide-mouthed, 250 mL capacity.

5.5. *Vacuum Flask*—1 L.

5.6. *Aspirator or Other Source of Vacuum*.

5.7. *Beakers*—assorted sizes.

5.8. *Bottles*—1 L minimum, amber, for storage of iodine and thiosulfate solutions.

5.9. *Glass-Stoppered Bottles*—1 L minimum, for storage of potassium iodate.

5.10. *Funnels*—100 mm top inside diameter.

5.11. *Buchner Funnel*—90 mm diameter.

5.12. *Filter Paper*—Grade 1, 11 µm, 90 mm diameter, cellulose, Whatman qualitative filter paper, or equivalent.

5.13. *Pipettes*—volumetric type, 5.0, 10.0, and 25.0 mL capacity.

5.14. *Volumetric Flasks*—1 L.

5.15. *Graduated Cylinders*—100 mL.

5.16. *Eyedropper*.

5.17. Mortar and Pestle.

5.18. 200 Mesh Sieve.

5.19. Magnetic Stirrer.

5.20. Hot Plate with Magnetic Stirrer.

5.21. *Drying Oven.*

X. Materials

X.1. *Coal Fly Ash*—a grab sample, regular sample, or composite sample as described in ASTM C311, Sections 6.1–6.3.

10. Procedure

10.1. Take a 500.0 mL volume of the solution prepared in Step 9.1 and perform a 3:1 dilution with three parts distilled water to produce a 0.025 N sodium thiosulfate solution.

10.2. Take a 500.0 mL volume of the solution prepared in Step 9.2 and perform a 3:1 dilution with three parts distilled water to produce a 0.025 N iodine solution.

10.3. Obtain a 300 to 400 g sample of the coal fly ash to be tested (See added section on Materials). This sample is boiled for 5 min in a solution of 5% weight HCl. The total mass of boiling solution should be at least four times that of the coal fly ash to be treated to ensure the availability of enough HCl to remove all sulfur and acidify the fly ash. The coal fly ash is then filtered using Grade 1, 90 mm diameter, cellulose, qualitative filter paper, or any equivalent filter paper, and dried at 103°C to a constant weight.

10.3.1. After drying, it may be necessary to break up the treated coal fly ash using a mortar and pestle such that all of the material passes through a 200 mesh sieve.

Note 1: Due to the relatively low adsorption capacity of coal fly ash, large masses of coal fly ash are required to adsorb enough iodine to cause an accurately measurable reduction in the iodine solution concentration.

10.4. From the treated sample (Step 10.3) weigh 10, 20, 40, and 80 g of treated coal fly ash. These will be referred to as samples *a*, *b*, *c*, and *d*, respectively. Record their respective weights to 0.001 g as $M_{FA(a)}$, $M_{FA(b)}$, $M_{FA(c)}$, and $M_{FA(d)}$.

10.4.1. The quantities specified in Step 10.4 are sufficient for most types of coal fly ash. In the case of very high carbon coal fly ash, or high activity coal fly ash, smaller quantities of treated sample may be required. This is readily determined by observing the solution color in Step 10.6 as the coal fly ash is added. If adding the coal fly ash causes the solution to become clear, the quantity added is in excess of the amount required (i.e., it has adsorbed all available iodine from solution).

10.4.2. It is recommended that Steps 10.6–10.9 be conducted first with the 10 g sample, then the 20 g sample, etc. If a level of treated sample addition results in the situation described in Step 10.4.1, use treated sample weights that reduce by a factor of 2 from the lowest successful test. Example: If 10 g and 20 g are both adequate, but 40 g is in excess, then use 5 g and 2.5 g samples to complete the series of four tests.

10.4.3. It is recommended that four different weights of treated coal fly ash be reacted with iodine solution, resulting in four data points to establish the adsorption isotherm.

10.5. Prepare vacuum flask, Buchner funnel, and Grade 1 90 mm diameter filter paper.

10.6. Starting with treated coal fly ash sample a, place the treated coal fly ash sample in a 250 mL Erlenmeyer flask and add 100.0 mL of the 0.025 N iodine solution (Step 10.2). Close the flask to minimize iodine volatilization. Place the flask on a stirring plate and stir the mixture for 5 min.

10.7. Quickly filter the mixture from Step 10.6.

10.8. Transfer the filtrate to a graduated cylinder and determine the volume of filtrate. Record this as the respective final iodine solution volume (V_f).

10.9. From the captured filtrate (Step 10.8), use the first 10 to 20 mL to rinse a pipette. Discard the rinse portions. Use clean beakers to collect the remaining filtrate. Mix each filtrate by swirling the beaker and then pipette 25.0 mL of each filtrate into a clean 250 mL Erlenmeyer flask. Titrate the filtrate with the standardized 0.025 N sodium thiosulfate solution (Step 10.1) until the solution is a pale yellow. Add approximately 0.5 mL of the starch indicator solution (Step 8.5) with an eye dropper and continue the titration with sodium thiosulfate until one drop produces a colorless solution. Record this as the respective volume of sodium thiosulfate used (V_T).

10.10. Repeat Steps 10.5–10.9 for the remaining three samples (e.g. 20, 40, and 80 g samples from Step 10.4)

11. Calculation

11.1 For each treated coal fly ash sample *a–d* (i.e. $M_{FA(a)}$, $M_{FA(b)}$, $M_{FA(c)}$, $M_{FA(d)}$), determine a corresponding solid phase iodine concentration (i.e., $q_{FA(a)}$, $q_{FA(b)}$, $q_{FA(c)}$, $q_{FA(d)}$) using the equation:

$$q_{FA} = \frac{[V_0 \times C_0] - [V_f \times C_f]}{M_{FA}} \quad (3)$$

where:

q_{FA} = solid phase iodine concentration (mg $_{\text{iodine}}$ / g $_{\text{fly ash}}$)
V_0 = initial iodine solution volume (L)
C_0 = initial iodine solution concentration (mg / L)
V_f = final iodine solution volume (L)
C_f = final iodine solution concentration (mg / L)
M_{FA} = mass of fly ash (g)

Determine C_0 as:

$$C_0 = N_2 \times 126930 \quad (4)$$

Determine Cf as:

$$C_f = \frac{V_T \times C_0}{25} \quad (5)$$

11.2 For each solid phase iodine concentration (i.e., $q_{FA(a)}$, $q_{FA(b)}$, $q_{FA(c)}$, $q_{FA(d)}$), determine a corresponding solution normality (i.e., $N_{FA(a)}$, $N_{FA(b)}$, $N_{FA(c)}$, $N_{FA(d)}$) using the equation:

$$N_{FA} = \frac{V_T \times N_2}{25} \quad (6)$$

11.3 Using a log-log plotting method, plot the four respective values of N_{FA} (*x*-axis) versus q_{FA} (*y*-axis). Fit a straight line to the four data points in the plot. An example is shown in Figure 1.

11.4 Using the plot produced in Step 11.3, enter the plot at a normality value (*x*-axis) of 0.01 and read the corresponding *y*-axis value (q).

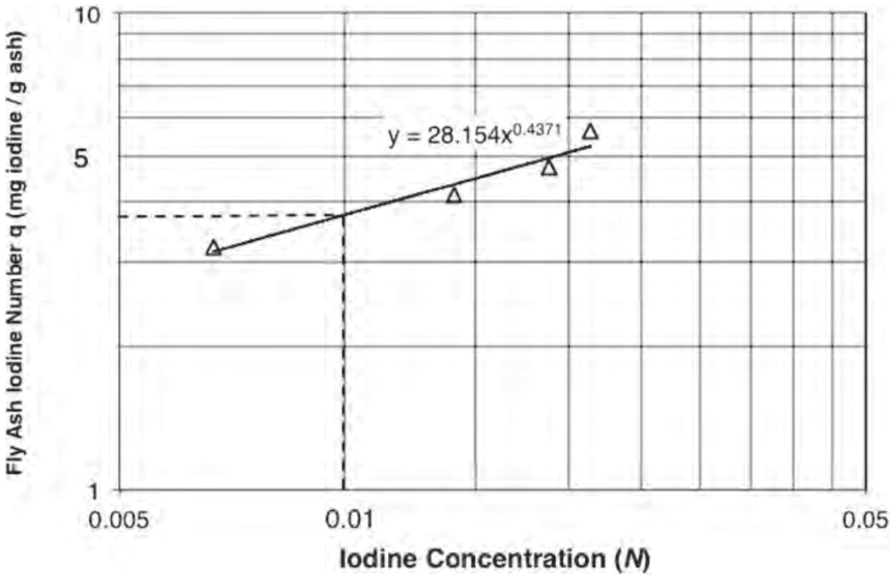

Figure 1. Example of iodine adsorption isotherm for coal fly ash.

12. Report

12.1. The reports should include the following:

- 12.1.1. Time and date of test
- 12.1.2. Fly ash source tested
- 12.1.3. Iodine number determined

Proposed Method of Test for

Determination of Air-Entraining Admixture Adsorption by Coal Fly Ash

1. SCOPE

1.1. This test method covers the determination of the quantity of air-entraining admixture (AEA) adsorbed by coal fly ash from an aqueous solution. The result is expressed as the volume of air-entraining admixture adsorbed per unit mass of coal fly ash (mL AEA/g fly ash). The quantity of air-entraining admixture adsorbed is a function of the solution air-entraining admixture concentration.

1.2. *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations to use.*

2. REFERENCED DOCUMENTS

2.1. *ASTM Standards*:

- D2652, *Standard Terminology Relating to Activated Carbon*
- C311, *Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete*
- D3860, *Standard Practice for Determination of Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique*

3. TERMINOLOGY

3.1. The terms used in this specification relative to activated carbon are defined in ASTM D2652.

4. SUMMARY OF TEST METHOD

4.1. The determination is based upon a three-point direct adsorption isotherm similar to that described in ASTM D3860. The isotherm provides a direct measurement of the amount of air-entraining admixture adsorbed by a coal fly ash.

4.2. A direct adsorption isotherm is determined by equilibrating mixtures of cement, fly ash, and air-entraining admixture solutions to determine the reduction in air-entraining admixture aqueous phase concentration due to adsorption by coal fly ash.

4.3. Portland cement is added to the system to account for the air-entraining admixture that is chemisorbed by the portland cement in a concrete mixture. A system that contains only cement and air-entraining admixture is utilized as a blank to determine the aqueous phase concentration of air-entraining admixture after chemisorption takes place. This aqueous phase concentration is considered to be the initial aqueous phase concentration. The reduction in this concentration resulting from the addition of coal fly ash to the system is used to determine the mass of air-entraining admixture adsorbed by fly ash.

4.4. The coal fly ash adsorption capacity is determined by dividing the mass of air-entraining admixture adsorbed from the solution by the mass of coal fly ash utilized in determining the isotherm point. Multiple isotherm points are obtained by varying the concentration of the air-entraining admixture solution. The isotherm points are analyzed using the Freundlich isotherm model that describes the correlation between solid phase (coal fly ash) capacity and the equilibrium air-entraining admixture aqueous phase concentration.

4.5. A test for chemical oxygen demand (mg COD/L) is used to determine the concentration of air-entraining admixture in solution.

4.6. The concentration of air-entraining admixture in the solution affects the capacity of a coal fly ash for air-entraining admixture adsorption.

4.7. The required apparatus consists of various laboratory glassware used to prepare solutions and contact coal fly ash with the air-entraining admixture solutions. Filtration equipment is also required. A spectrophotometric method is employed to determine COD.

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5. SIGNIFICANCE AND USE

5.1. The partitioning of an air-entraining admixture among the various solid phases in a concrete mixture is identified and quantified using this direct adsorption isotherm test method. Direct adsorption isotherms quantify the interaction between coal fly ash and an air-entraining admixture.

5.2. An isotherm provides a quantitative measurement of the amount of air-entraining admixture adsorbed by a coal fly ash, which can be used to predict and adjust the dosage of air-entraining admixture, relative to a baseline dosage used for a concrete mixture with no coal fly ash, to compensate for the air-entraining admixture adsorbed when a coal fly ash is added or substituted into the concrete mixture.

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6. APPARATUS

6.1. *Analytical Balance*—accuracy ± 0.01 g.

6.2. *Flasks*—Erlenmeyer 250 mL capacity with a ground-glass stopper or rubber stopper.

6.3. *Volumetric Flasks*—200 mL and 1 L.

6.4. *Vacuum Flask*—1 L.

6.5. *Aspirator or Other Source of Vacuum.*

6.6. *Buchner Funnel*—90 mm top inside diameter.

6.7. *Filter Paper*—Grade 1, 11 µm, 90 mm diameter, cellulose, Whatman qualitative filter paper, or equivalent.

6.8. *Pipettes*—volumetric type, 2.0 mL capacity.

6.9. *Graduated Cylinders*—100 and 200 mL.

6.10. *Magnetic Stirrer.*

6.11. *Drying Oven.*

6.12. *COD Determination Test Kit*— HACH Method 8000, high-range COD or equivalent.

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7. REAGENTS

7.1. *Water*—distilled or reagent water.

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8. MATERIALS

8.1. *Coal Fly Ash*—a grab sample, regular sample, or composite sample as described in C311, Sections 6.1–6.3.

8.2. *Portland Cement*—Select the specific cement to be used with the coal fly ash (Step 8.1) and air-entraining admixture (Step 8.3) in any concrete mixture. If the specific portland cement is unavailable, a portland cement of the same type (i.e., AASHTO M 85 type) and similar composition and Blaine fineness may be substituted, but the performance of the air-entraining admixture predicted by this test method may vary.

8.3. *Air-Entraining Admixture*—Select the specific air-entraining admixture to be used with the coal fly ash (Step 8.1) and portland cement (Step 8.2) in any concrete mixture.

9. MEASUREMENT OF CHEMICAL OXYGEN DEMAND

9.1. The concentration of air-entraining admixture in solution is determined by measuring the solution chemical oxygen demand (COD), expressed in mg COD/L.

9.2. Standard procedures for measuring COD are given in *Standard Methods for the Examination of Water and Wastewater*[1]. Two specific methods are described: 5220C closed reflux titrimetric method and 5220D closed reflux colorimetric method. Either method is acceptable. Method 5220D closed reflux colorimetric method is recommended.

9.3. Kits are commercially available to facilitate performing the 5220D closed reflux colorimetric method, as described in Section 6.

10. PREPARATION OF SOLUTIONS

10.1. There are no specific solution strengths required to perform the test. To accurately determine COD, it is recommended that three solution strengths (i.e., solutions i, ii, and iii) be selected that result in COD falling in the range of 300 to 1300 mg COD/L after aliquots of the solutions have equilibrated with 20 g of portland cement. These will be used to determine isotherm points i, ii, and iii, respectively.

Note 1—In most cases AEA solutions having concentrations of 5, 10, and 20 mL/L will produce COD_{BK} measurement (Step 10.3.11) between 100 and 1300 mg COD /L after equilibrating with 20 g of the portland cement.

Note 2—If laboratory facilities permit, all three solutions or coal fly ash/portland cement/solution combinations can be reacted simultaneously. The procedure described herein assumes each solution or each coal fly ash/portland cement/solution combination will be reacted synchronously rather than simultaneously.

10.2. The relationship between air-entraining admixture concentration and COD must be determined separately for each different air-entraining admixture type to be evaluated.

10.3. *Determine the COD/Air-Entraining Admixture Solution Concentrations:*

10.3.1. Assemble and prepare the vacuum filter apparatus.

10.3.2. Measure 5 mL of air-entraining admixture using a graduated cylinder.

10.3.3. Add the air-entraining admixture to a 1 L volumetric flask and dilute the air-entraining admixture with distilled water to a total solution volume of 1 L.

10.3.4. Record the initial solution concentration (C_{0i}) in mL AEA/L.

10.3.5. Measure 200 mL of the air-entraining admixture solution.

10.3.6. Weigh 20 g of portland cement and record to nearest 0.01g (M_{PCi}).

10.3.7. Combine the 200 mL of air-entraining admixture solution with 20 g of portland cement in a 250 mL Erlenmeyer flask. Add a magnetic stirring bar and stopper the flask.

10.3.8. Stir for 60 ± 2 min using a stir speed sufficient to keep the solids in suspension. If necessary, use a glass rod to initiate stirring.

10.3.9. Remove the solution and portland cement from the stirrer and filter. If vacuum is lost as a result of cracks forming in the filter cake, use a spatula to close the cracks. Filter until filtrate is produced at a rate of approximately 1 drop every 10 s.

10.3.10. Transfer the filtrate to a graduated cylinder and determine the volume of filtrate in liters (L). Record this as the respective final solution volume (V_{BKi}).

10.3.11. Determine the COD of the final solution and record this as COD_{BKi}.

10.3.12. If the COD_{BKi} is less than 100 mg COD/L or greater than 1300 mg COD/L, estimate by ratio the required air-entraining admixture volume to achieve a COD_{BKi} of approximately 800 mg COD/L and repeat Steps 10.3.3–10.3.11.

10.3.13. Based upon the results of Step 10.3.11, estimate by ratio the air-entraining admixture volume required to prepare solutions ii and iii with final solution concentrations (i.e., solution concentration after contact with the portland cement) such that together the three prepared solutions adequately cover the range of 100 to 1300 mg COD/L. Repeat Steps 10.3.3–10.3.10 to prepare solutions ii and iii and record M_{PCii}, M_{PCiii}, C_{0ii}, C_{0iii}, COD_{0ii}, COD_{0iii}, V_{Fii}, V_{Fiii}, COD_{BKii}, and COD_{BKiii}.

11. PROCEDURE

11.1. Obtain a 300 to 400 g sample of the coal fly ash to be tested (Step 8.1). Dry this sample to constant weight at a temperature of 110° ± 2° C.

11.2. Obtain a 300 to 400 g sample of the portland cement to be tested (Step 8.2).

11.3. Assemble and prepare the vacuum filter apparatus.

11.4. *Determine the COD Contribution from the Fly Ash:*

11.4.1. Measure 80 g of the coal fly ash and record this weight to 0.01 g (M_{FA*}).

11.4.2. Measure 200 mL of distilled water.

11.4.3. Combine the 80 g of coal fly ash and 200 mL of distilled water in a 250 mL Erlenmeyer flask. Add a magnetic stirring bar and stopper the flask.

11.4.4. Stir for 60 ± 2 min using a stir speed sufficient to keep the solids in suspension. If necessary, use a glass rod to initiate stirring.

11.4.5. Remove the slurry from the stirrer and filter. If vacuum is lost as a result of cracks forming in the filter cake, use a spatula to close the cracks. Filter until filtrate is produced at a rate of approximately 1 drop every 10 s.

11.4.6. Transfer the filtrate to a graduated cylinder and determine the volume of filtrate in liters (L). Record this as the respective final solution volume (V_{FA*})

11.4.7. Determine the COD of the final solution and record this as COD_{FA*}.

11.5. *Determine the COD Contribution from the Portland Cement:*

11.5.1. Measure 80 g of the portland cement and record this weight to 0.01 g (M_{PC*}).

11.5.2. Measure 200 mL of distilled water.

11.5.3. Combine the 80 g of portland cement and 200 mL of distilled water in a 250 mL Erlenmeyer flask. Add a magnetic stirring bar and stopper the flask.

11.5.4. Stir for 60 ± 2 min using a stir speed sufficient to keep the solids in suspension. If necessary, use a glass rod to initiate stirring.

11.5.5. Remove the slurry from the stirrer and filter. If vacuum is lost as a result of cracks forming in the filter cake, use a spatula to close the cracks. Filter until filtrate is produced at a rate of approximately 1 drop every 10 s.

11.5.6. Transfer the filtrate to a graduated cylinder and determine the volume of filtrate in liters (L). Record this as the respective final solution volume (V_{PC*})

11.5.7. Determine the COD of the final solution and record this as COD_{PC*}.

11.6. *Determine the COD of the Isotherm Data Points:*

11.6.1. Measure 200 mL of air-entraining admixture solution i

11.6.2. Measure 40 g of the coal fly ash to be tested. Record the weight to 0.01 g (M_{FAi}).

11.6.3. Measure 20 g of the portland cement to be tested. Record the weight to 0.01 g (M_{PCi}).

11.6.4. Combine the 200 mL of air-entraining admixture solution with the 40 g of coal fly ash (Step 11.6.2) and 20 g of portland cement in a 250 mL Erlenmeyer flask. Add magnetic stirring bar and stopper the flask.

11.6.5. Stir for 60 ± 2 min using a stir speed sufficient to keep the solids in suspension.

11.6.6. Remove the slurry from the stirrer and filter. If vacuum is lost as a result of cracks forming in the filter cake, use a spatula to close the cracks. Filter until filtrate is produced at a rate of approximately 1 drop every 10 s.

11.6.7. Transfer the filtrate to a graduated cylinder and determine the volume of filtrate in liters (L). Record this as the respective final solution volume (V_{FCi}).

11.6.8. Determine the COD of the final solution and record this as COD_{FCi}.

11.6.9. Repeat Steps 11.6.1–11.6.8 for solutions ii and iii.

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12. CALCULATION

12.1. *Determine the Coal Fly Ash Capacity (q) at Each Solution Strength:*

Capacity for solutions *(mL air entraining admixture / g coal fly ash)* (repeat for solutions ii and iii):

$$q_i = \left[\frac{(V_{BKi} \times COD_{BKi})}{M_{FAi}} - \frac{(V_{FCi} \times COD_{FCi})}{M_{FAi}} + \frac{(V_{FA*} \times COD_{FA*})}{M_{FA*}}\right] \times \frac{C_{0i}}{\left(COD_{BKi} - (COD_{PC*}) \times \left(\frac{M_{PCi}}{M_{PC*}}\right)\right)} \tag{1}$$

12.2. *Determine Final Air-Entraining Admixture Concentration in Water*

$$C_{Fi} = \left[COD_{FCi} - \frac{(COD_{FA*} \times M_{FAi})}{M_{FA*}} - \frac{(COD_{PC*} \times M_{PCi})}{M_{PC*}}\right] \times \frac{0.1 \times C_{0i}}{\left(COD_{BKi} - (COD_{PC*}) \times \left(\frac{M_{PCi}}{M_{PC*}}\right)\right)} \tag{2}$$

Determine the final air-entraining admixture concentration in water for solutions ii and iii, substituting in the associated values for those determinations.

12.3. *Plot Solution Concentration versus Capacity:*

Plot the results using a log-log scale. Plot the solution concentration (i.e., C_{0i}, C_{0ii}, C_{0iii}) on the *x*-axis and capacity (i.e., q_i, q_{ii}, q_{iii}) on the *y*-axis.

Fit a power line to the data, the equation for which can be used to determine the volume of air-entraining admixture adsorbed per gram of coal fly ash, as a function of the air-entraining admixture concentration.

An example plot is shown in Figure 1.

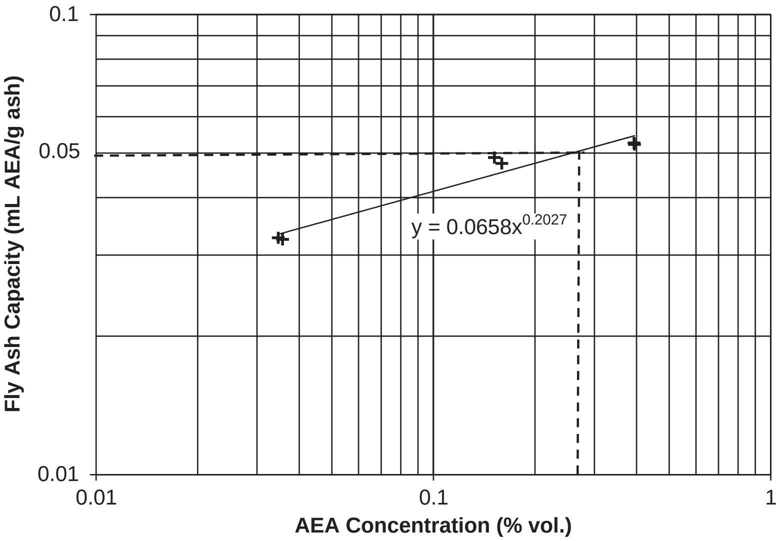

Figure 1. Example of direct adsorption isotherm for coal fly ash.

12.4. To use the graph, calculate the air-entraining admixture dosage for a concrete mixture design in terms of percentage of air-entraining admixture by volume. Enter the graph on the *x*-axis at the determined percentage of air-entraining admixture by volume. Intercept the isotherm line and read off the corresponding fly ash capacity on the *y*-axis. The capacity determined is the volume of air-entraining admixture that will be adsorbed per gram of fly ash.

12.5. An example calculation is shown below:

Concrete Mix Design Parameters:

Item	**Quantity**	
	Customary Units	**Converted Units**
Water	290 lb	34.8 gal
Air-Entraining Admixture	11.5 fl oz	0.09 gal

Assume 100 lb (45.4 kg) of fly ash is substituted for 100 lb of portland cement.

$$\text{Volume \% Air-Entraining Admixture} = \frac{0.09 \text{ gal Air-Entraining Admixture}}{34.8 \text{ gal water}} \times 100 = 0.26 \text{ volume \%}$$

From Figure 1, fly ash capacity = 0.05 mL air-entraining admixture per gram coal fly ash

$$\frac{0.05 \text{ mL air-entraining admixture}}{\text{g coal fly ash}} \times \frac{45.4 \text{ kg coal fly ash}}{} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 2270 \text{ mL air-entraining admixture}$$

$$2270 \text{ mL air-entraining admixture} \times \frac{1 \text{ fl oz}}{29.57 \text{ mL}} = 76.8 \text{ fl oz}$$

In this example, it is estimated 100 lb of coal fly ash has the capacity of 76.8 fl oz of air-entraining admixture.

13. REPORT

13.1. Report the following information

- Time and date of test
- Fly ash source tested
- Cement source tested
- Air-entraining admixture tested
- Coal fly ash capacity plot and power fit equation for the adsorption isotherm

14. PRECISION AND BIAS

14.1. *Precision*—To be determined.

14.2. *Bias*—There is no accepted standard sample that can be used to establish bias.

15. KEYWORDS

15.1. Coal fly ash; air-entraining admixture; direct adsorption isotherm.

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[1] Eaton, A. D., L. S. Clesceri, E. W. Rice, A. E. Greenberg, and M. H. Franson, eds. *Standard Methods for the Examination of Water and Wastewater*, 21st ed., Port City Press, Baltimore, Md., 2005, pp. 4-58 to 4-60. ISBN 0-87553-047-8.

ATTACHMENT C

Details of the Research into Methods for Evaluating Fly Ash Use in Highway Concrete (NCHRP Project 18-13)

This attachment is not published herein but is available by searching for “NCHRP Report 749” on the TRB website (http://www.trb.org).

Abbreviations and acronyms used without definitions in TRB publications:

A4A	Airlines for America
AAAE	American Association of Airport Executives
AASHO	American Association of State Highway Officials
AASHTO	American Association of State Highway and Transportation Officials
ACI–NA	Airports Council International–North America
ACRP	Airport Cooperative Research Program
ADA	Americans with Disabilities Act
APTA	American Public Transportation Association
ASCE	American Society of Civil Engineers
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
ATA	American Trucking Associations
CTAA	Community Transportation Association of America
CTBSSP	Commercial Truck and Bus Safety Synthesis Program
DHS	Department of Homeland Security
DOE	Department of Energy
EPA	Environmental Protection Agency
FAA	Federal Aviation Administration
FHWA	Federal Highway Administration
FMCSA	Federal Motor Carrier Safety Administration
FRA	Federal Railroad Administration
FTA	Federal Transit Administration
HMCRP	Hazardous Materials Cooperative Research Program
IEEE	Institute of Electrical and Electronics Engineers
ISTEA	Intermodal Surface Transportation Efficiency Act of 1991
ITE	Institute of Transportation Engineers
MAP-21	Moving Ahead for Progress in the 21st Century Act (2012)
NASA	National Aeronautics and Space Administration
NASAO	National Association of State Aviation Officials
NCFRP	National Cooperative Freight Research Program
NCHRP	National Cooperative Highway Research Program
NHTSA	National Highway Traffic Safety Administration
NTSB	National Transportation Safety Board
PHMSA	Pipeline and Hazardous Materials Safety Administration
RITA	Research and Innovative Technology Administration
SAE	Society of Automotive Engineers
SAFETEA-LU	Safe, Accountable, Flexible, Efficient Transportation Equity Act: A Legacy for Users (2005)
TCRP	Transit Cooperative Research Program
TEA-21	Transportation Equity Act for the 21st Century (1998)
TRB	Transportation Research Board
TSA	Transportation Security Administration
U.S.DOT	United States Department of Transportation