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CHARACTERIZATION OF A COAL FLY ASH-CEMENT SLURRY BY THE ABSOLUTE FOAM INDEX

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CHARACTERIZATION OF A COAL FLY ASH-CEMENT SLURRY BY THE ABSOLUTE FOAM INDEX

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Preface

The work in this dissertation was completed as part of a research project funded by the National Cooperative Highway Research Program (NCHRP) of the Transportation Research Board of The National Academies: Project 18-13: Specifications and Protocols for Acceptance Tests of Fly Ash Used in Highway Concrete with the exception of the correlations in Chapter 4 as they succeeded the project. The data in Chapters 2 and 3 has been submitted to NCHRP previously. An invention disclosure for the test itself has been submitted to Michigan Tech Department of Innovation and Industry Engagement and a draft has been submitted to NCHRP as this work was performed in conjunction with the American Association of State Highway Transportation and Transportation Officials (AASHTO). Chapters 2, 3, and 4 are presented in their expanded form as the body of this dissertation and will be condensed and submitted to journals for publication.

Chapter 2, Characterization of Coal Fly Ash by the Absolute Foam Index: The dissertation author conducted the literature review and was assisted with analysis and data collection by Dr. Zeyad Ahmed, Dr. David Hand, and Amanda Hartman. The dissertation author is the primary author.

Chapter 3, A Standard Test Procedure for Absolute Foam Index Test for Coal Fly Ash: Test procedures were formulated by the dissertation author, Dr. Zeyad Ahmed, and Dr. David Hand. The dissertation author conducted the analysis and was assisted with the data collection by Dr. Zeyad Ahmed and Amanda Hartman. The dissertation author is the primary author. Dr. David Watkins is acknowledged for guidance provided for the statistical analysis.

Chapter 4, Foam Index Test Results Correlations to Equilibrium Isotherms & Mortar Air: Test correlations were formulated by the dissertation author, Dr. Zeyad Ahmed, and Dr. David Hand. The dissertation author collected data and was assisted with the data collection by Dr. Zeyad Ahmed. The dissertation author conducted the analysis. The

dissertation author is the primary author. Dr. Lawrence Sutter is acknowledged for oversight of undergraduate Benjamin Longmire who collected mortar data. Dr. Jarslow Drelich is acknowledged for guidance provided for the critical micelle determination.

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The authoring of this publication herein was performed by myself, Melanie Kueber Watkins, as partial requirements for a Doctor of Philosophy in Civil Engineering.

This study was sponsored by the American Association of State Highway and Transportation Officials in cooperation with the Federal Highway Administration, and was conducted as part of the National Cooperative Highway Research Program Project 18-13, which is administered by the Transportation Research Board of the National Research Council, Senior Program Officer A. Hanna with the exception of the correlations in Chapter 4, as the correlations in Chapter 4 succeeded the project. The publication of this research does not necessarily indicate acceptance by the National Academies, the Federal Highway Administration, or by the American Association of State Highway Officials of the findings, conclusions, or recommendations either inferred or specifically expressed herein. The draft final report containing data from chapters 2 and 3 for Project 18-13 has been submitted to NCHRP in September 2012. Dr. David Hand, Professor of Civil and Environmental Engineering at MTU and Dr. Zeyad Ahmed provided intellectual guidance for the analysis herein. The analysis herein was performed by myself and the data collection was performed by myself with help from Dr. Zeyad Ahmed, Amanda Hartman, and Benjamin Longmire. I would like to thank NCHRP for their cooperation and support of the project. I would like to thank the Michigan Tech Department of Civil and Environmental Engineering, the University Transportation Center, and the National Science Foundation Integrative Graduate Education Research Traineeship for providing my funding. A special thanks to Ms. Amanda Hartman and Dr. Jarslow Drelich for their help with laboratory experiments, Dr. David W. Watkins for his help with statistical analysis, and Mrs. Evelyn Johnson, Dr. David W. Watkins, and Mr. Shaughn Kern for reviewing drafts. I would like to thank my committee members Dr. Jarslow Drelich, Dr. James Wood, and Dr. Eric Seagren for valuable suggestions and taking interest in my work.

Definitions

Absolute volume of AEA or absolute foam index – the volume of undiluted AEA solution added for a 15-second stable foam. This includes the solution concentration.

Concentration – ml of stock AEA/ml of solution, expressed as %.

Dosage – amount of AEA stock solution added to a mortar or concrete mixture. Expressed in g of AEA, ml of AEA/kg of cementitious, or as a concenration in ml of stock AEA/ml of solution.

Fly ash (FA) – all the fly ash used for the work in this entire document was generated from coal combustion; *coal fly ash*. The terms 'fly ash (FA)' or 'ash' as used herein, are synonymous to coal fly ash in this document. It is possible that the test data herein correlates to other types of ash, but it is recommended that tests that tests be completed for verification.

Foam Index – total amount of AEA solution in ml required to achieve a metastable foam.

Abbreviations

AASHTO – American Association of State Highway Transportation Officials

AEA – Air-entraining admixture

ASTM – American Society of Testing Materials

CMC – Critical micelle concentration

COV – Coefficient of variation

LOI, LOI % – Loss on ignition, loss on ignition %

FA – Coal fly ash as used herein

FI – Foam index

FHWA – Federal Highway Administration

NCHRP – National Cooperative Highway Research Program

WAS – Wrist Action Shaker

Abstract

This dissertation established a standard foam index: the absolute foam index test. This test characterized a wide range of coal fly ash by the absolute volume of air-entraining admixture (AEA) necessary to produce a 15-second metastable foam in a coal fly ash-cement slurry in a specified time.

The absolute foam index test was used to characterize fly ash samples having loss on ignition (LOI) values that ranged from 0.17 to 23.3 %wt. The absolute foam index characterized the fly ash samples by absolute volume of AEA, defined as the amount of undiluted AEA solution added to obtain a 15-minute endpoint signified by 15-second metastable foam. Results were compared from several foam index test time trials that used different initial test concentrations to reach termination at selected times. Based on the coefficient of variation (CV), a 15-minute endpoint, with limits of 12 to 18 minutes was chosen. Various initial test concentrations were used to accomplish consistent contact times and concentration gradients for the 15-minute test endpoint for the fly ash samples.

A set of four standard concentrations for the absolute foam index test were defined by regression analyses and a procedure simplifying the test process. The set of standard concentrations for the absolute foam index test was determined by analyzing experimental results of 80 tests on coal fly ashes with loss on ignition (LOI) values ranging from 0.39 to 23.3 wt.%. A regression analysis informed selection of four concentrations (2, 6, 10, and 15 vol.% AEA) that are expected to accommodate fly ashes with 0.39 to 23.3 wt.% LOI, depending on the AEA type. Higher concentrations should be used for high-LOI fly ash when necessary. A procedure developed using these standard concentrations is expected to require only 1-3 trials to meet specified endpoint criteria for most fly ashes.

The AEA solution concentration that achieved the metastable foam in the foam index test was compared to the AEA equilibrium concentration obtained from the direct adsorption

isotherm test with the same fly ash. The results showed that the AEA concentration that satisfied the absolute foam index test was much less than the equilibrium concentration. This indicated that the absolute foam index test was not at or near equilibrium. Rather, it was a dynamic test where the time of the test played an important role in the results. Even though the absolute foam index was not an equilibrium condition, a correlation was made between the absolute foam index and adsorption isotherms.

Equilibrium isotherm equations obtained from direct isotherm tests were used to calculate the equilibrium concentrations and capacities of fly ash from 0.17 to 10.5% LOI. The results showed that the calculated fly ash capacity was much less than capacities obtained from isotherm tests that were conducted with higher initial concentrations. This indicated that the absolute foam index was not equilibrium. Rather, the test is dynamic where the time of the test played an important role in the results. Even though the absolute foam index was not an equilibrium condition, a correlation was made between the absolute foam index and adsorption isotherms for fly ash of 0.17 to 10.5% LOI.

Several batches of mortars were mixed for the same fly ash type increasing only the AEA concentration (dosage) in each subsequent batch. Mortar air test results for each batch showed for each increase in AEA concentration, air contents increased until a point where the next increase in AEA concentration resulted in no increase in air content. This was maximum air content that could be achieved by the particular mortar system; the system reached its air capacity at the saturation limit. This concentration of AEA was compared to the critical micelle concentration (CMC) for the AEA and the absolute foam index.

1. Introduction

Beneficial use of coal fly ash as a replacement for portland cement in concrete in the United States has been documented as early as the 1930s (FHWA 2011, UND EERC n.d., Davis et al. 1937). The American Coal Ash Association reported that approximately 68 million tons of fly ash was produced in the United States in 2010 of which 38% was beneficially used (ACAA 2010). The major use, only 16%, was as a supplementary cementitious material in concrete (ACAA 2010). The ACAA statistics show that production and use have increased since 2000 when 63 million tons were produced with 31% beneficially reused, but approximately the same percentage, 17%, was used in concrete (ACAA 2010).

Specifications for fly ash written by the American Association of State Highway Transportation Officials (AASHTO), AASHTO M 295-11 *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete* and those written by American Society of Testing and Materials (ASTM), ASTM C618-08a *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, specify minimums or maximums of certain chemical compositions that coal fly ash must meet instead of addressing performance in fresh and hardened concrete (Sutter, et. al 2013).

The main chemical requirement specified by AASHTO M 295-11 and ASTM C618-07 that this research is related to is loss on ignition % (LOI %) (AASHTO 2011, ASTM 2008) which has been used as an indicator of carbon content by loss of mass at 750°F (ASTM 2011, Harris et al. 2006). These requirements specify that fly ash must meet minimums of 5.0% and 6.0% LOI respectively. ASTM C618-08a also includes a clause that states coal fly ash with up to 12% LOI [Class F] can be used if records and tests deem it acceptable (ASTM 2008). Increased beneficial use as a supplementary cementitious material is affected by the prescriptive nature of the LOI specification because it does not predict coal fly ash performance (Külaots et al. 2003) in regards to fly ash interactions with air-entraining admixtures (AEAs), which are used in concrete to aid with freeze thaw resistance (Külaots et al. 2003, Hewlett 2004, Sutter, et. al 2013).

Air-entraining admixtures are surfactants that are added to a fresh concrete mixture to capture air from various mechanisms occurring in the mixture, including mixing and hydration reactions that occur when finely ground cement is mixed with water to form solid concrete (Dodson 1990, Du and Folliard 2005, Hewlett 2004). These air voids form spaces for migratory water to retreat and expand when ambient temperatures fall below the freezing point (Benazzouk et al. 2006, Du and Folliard 2005, Hewlett 2004, Külaots et al. 2003). The increased air void content at the proper spacing increases freeze thaw resistance of the concrete (Du and Folliard 2005, Hewlett 2004).

Coal fly ash may also contain organic carbon that creates an unfavorable condition for an AEA. When coal fly ash is added as a supplementary cementitious material to a fresh concrete, mortar, or paste mixture, its organic carbon adsorbs the air-entraining admixture and making it unavailable to stabilize air in the fresh matrix (Külaots et al. 2003; Pedersen et al. 2008).

AEA molecules have an affinity for adsorption by organic fly ash carbon. The structure of an air-entraining admixture [or surfactant] molecule is described as having a polar, hydrophilic head and a non-polar, hydrophobic tail (Dodson 1990, Du and Folliard 2005).

Air is entrained or captured in a fresh cement paste when the hydrophobic head of the air-entraining admixture is adsorbed to the cement particles leaving the non-polar hydrophobic tails available to adhere to the air. A sufficient amount of air-entraining admixture must be available in the paste solution to adhere to the air (Bruere 1955, Du and Folliard 2005)

In a fresh mixture where coal fly ash is present, the hydrophobic tails of the surfactant have a stronger affinity to the fly ash organic carbon than the air, and the surfactant is adsorbed by the organic carbon sites. The surfactant molecules and carbon pores are 10^7 times smaller than the carbon particles (Hachmann et al. 1998, Pedersen et al. 2008).

A compensating amount of AEA can be added to the fresh concrete but presently a standard test that can predict the total amount needed to fulfill the sites on the coal fly ash carbon and to capture air in the concrete mixture is not available (Pedersen et al. 2008). Coal fly ash may meet the ASTM or AASHTO maximum LOI, but LOI is not a measure of adsorption and does not predict the amount of AEA to fulfill the carbon adsorption sites (Pedersen et al. 2008). LOI does not always correlate to the amount of AEA because test results may error up to 75%; mass loss measured in the LOI test includes not only the loss due to carbon combustion but also to mass loss of portlandite, carbonate, bound water, and gains from iron and sulfur oxidation (Brown and Dykstra 1995, Dodson 1990). The inaccuracy in LOI may be additionally attributed to the fact that fly ash particle sizes range from greater than 355 μm to less than 45 μm (Külaots et al. 2004) and the larger particles have a potentially larger surface area exposed to the LOI test. It is important to note that this difference in surface area for the same LOI fly ashes may also create a difference in adsorption capacity (Külaots et al. 2004).

An alternative to the LOI test is the foam index test. The foam index test usually involves adding a specified amount of a dilute aqueous solution of AEA to a slurry of fly ash, cement, and water. After the addition, the slurry is agitated for a period of time specified by the procedure, and the slurry surface is then visually monitored for a "stable foam." If the foam is not stable after one "cycle" (i.e. addition of the AEA, agitation, and observation), then additional cycles continue with AEA additions incrementally added until a metastable foam forms. Foam stability is subjectively defined by the observer. In general, a metastable foam is defined as one that covers the entire surface of the slurry in the test container, and persists for the prescribed observation time without dissipating (Harris et al. 2008a, Külaots et al. 2003, Dodson 1990).

Recognizing a metastable foam can be time consuming and difficult for users, depending upon the ash type and AEA concentration used to complete the test. Producing a metastable foam can also be problematic as shaking intensity, frequency, and period varies among tests. Further, foams can look different based on the fly ash color. An additional complication is that cement typically forms a foam scum, making it difficult for the technician to identify a metastable foam caused by the AEA. At the point where the technician feels a metastable foam exists for the specified time, the known number of AEA increments and the AEA concentration are used to calculate the total amount of AEA required to achieve the stable foam. This is the foam index.

Standardizing the foam index test required a comprehensive understanding of the test mechanisms and its reliability. A literature review of available procedures was conducted in order to discern which tests offered variables that could produce uniform contact time. Agitation methods were investigated to maximize reproducibility. A standard procedure that successfully characterized a broad range of fly ash was established and tested by performing an error analysis and a sensitivity analysis. Additionally, foam index test correlations to the iodine number, direct adsorption isotherms, and mortar results are included.

1.1 Dissertation Objectives

Since LOI cannot accurately predict the amount of AEA adsorbed by fly ash carbon a goal of this research was to standardize a test called *the foam index test*, so that it could become a reliable predictive method for industry.

The reasons to standardize the foam index test are: 1) it is predictive of adsorption where the LOI test is not, because the environment created by the foam index test exposes coal fly ash to an AEA; 2) the foam index test is already used in industry and a standard procedure would increase the precision of test results and data interpretation would become unified across industry; 3) the test is simple, and uses readily available, simple equipment; and 4) correlation of the foam index to an AEA dosage is desired. Many procedures exist in literature (Harris 2007, Harris et al. 2008, 2008a, 2008b, Külaots et al. 2004). Preliminary studies to predict dosage for low fly carbon to date (Hill and Majors 2001, Harris et al. 2008, Pedersen et al. 2008) showed promise.

1.2 Dissertation Overview

The dissertation consists of three chapters that address the objectives of the research. These chapters are the body of this dissertation and will be condensed and submitted to journals for publication.

Chapter 2 focuses on concentration differences, agitation accuracy, and test reproducibility through two tests chosen from a review of 15 test procedures. Comparisons of test results for different test types and manual versus automated agitation were made. Different concentration strengths were evaluated and how differences in concentration effected test time. The most reproducible test was determined.

Chapter 3. A regression analysis was performed to model the test data using the foam index test variables: initial solution concentration of AEA, the time to test termination, and absolute volume of AEA required to produce metastable foam. A standard test procedure with optimum solution strengths was developed using a multiple regression analysis.

Chapter 4 discusses correlations of the absolute foam index to initial AEA adsorption isotherm concentrations, and mortar dosage for maximum air content on a volume per volume basis. The correlation to adsorption isotherms showed relationship to equilibrium. Mortar dosage for maximum air content was compared with mortar flow (slump) and the critical micelle concentration. Mortar dosage was compared with absolute foam index.

Chapter 5 concludes research results and includes recommendations for future research.

1.3 Materials Introduction

1.3.1 Materials

Materials chosen to develop the absolute foam index test as listed herein were in accordance with National Cooperative Highway Research Program (NCHRP) of the Transportation Research Board of The National Academies: Project 18-13: Specifications and Protocols for Acceptance Tests of Fly Ash Used in Highway Concrete (Sutter, et. al 2013).

1.3.1.1 Coal Fly Ash and Cement

Coal fly ash used throughout this study ranged from 0.17 to 23.3% LOI. The fly ash used was representative of the range available for use in transportation infrastructure construction in the United States. The cement used was Lafarge Type I/II cement (Alpena, MI). The cementitious materials were characterized according to ASTM C618-08a *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete* (ASTM 2008) either as a part NCHRP Project 18-13 or materials suppliers. Complete chemical data is shown in Table 1.1. Suitable fly ash sources chosen from the materials in Table 1.1 were used where appropriate throughout this study and identified throughout.

Table 1.1

Chemical composition of fly ash and cement.

Fly Ash ID	Class	LOI (% wt.)	SiO_2 (% wt.)	Al_2O_3 (% wt.)	Fe_2O_3 (% wt.)	CaO (%wt.)	SO_3 (%wt.)	MgO (%wt.)
FA- H (8)	F	0.17	60.9	25.7	4.66	3.46	0.29	1.12
FA-T (20)	F	0.39	44.8	23.1	9.51	13.6	0.96	2.97
FA - A (1)	F	0.87	61.6	27.9	3.02	0.82	n/a	n/a
FA-ZG	C	1.22	37.2	19.2	4.74	19.19	2.3	4.68
FA-J (10)	F	1.26	46.0	23.6	22.3	1.28	0.77	0.99
FA- O (15)	F	1.43	58.9	16.2	4.71	10.2	0.86	3.13
FA-G (7)	F	2.25	53.9	27.7	8.29	1.45	0.29	1.12
FA- ZN (40)	F	3.35	53.9	26.3	6.24	9.1	1.1	2.28
FA-ZF (32)	F	6.06	58.7	29.25	5.34	0.99	0.03	0.87
FA 100	F	10.37	54.1	26.56	5.06	1.49	0.17	0.65
FA-ZM (39)	F	10.49	39.6	20	12.7	9.1	1.1	2.28
FA 101	F	14.68	49.53	23.88	4.77	2.0	0.32	0.44
FA 102	F	18.99	44.97	21.19	4.49	2.50	0.46	0.22
FA-ZJ (36)	F	21.34	NA	NA	NA	NA	NA	NA
FA-ZE (31)	F	23.3	40.4	18.5	4.2	3	0.6	NA
Lafarge Type I/II (PC-1)		1.37	20.1	4.7	2.7	6.9	2.6	2.4

1.3.1.2 Air-entraining Admixtures.

Five AEAs, of four different surfactant types, were used in this study. These were representative of the range of AEAs used in highway concrete. These AEAs are commonly used throughout the concrete industry. The AEAs are shown in Table 1.2.

Table 1.2

AEAs and chemical information.

Surfactant ID	Surfactant Type
AEA-A	Vinsol Resin
AEA-B	Alpha Olefin Sulfonate
AEA-E	Benzene Sulfonate
AEA-D	Resin/Rosin/Fatty Acid
AEA-C	Resin/Rosin/Fatty Acid

1.4 References

AASHTO. 2011. AASHTO M 295-11 Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. American Association of State Highway and Transportation Officials, Washington, D.C.

ACAA. 2010. ACAA 2010 Coal Combustion Product (CCP) Production and Use Survey Report. [cited: January 16, 2012] Available from: http://acaa.affiniscape.com/associations/8003/files/2010_CCP_Survey_FINAL_102011.pdf

ASTM. 2011. ASTM C311-11a Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete. Annual Book of ASTM Standards. Volume 4.02 Concrete and Aggregates. American Society for Testing and Materials, West Conshohocken, PA.

ASTM. 2008. C618-08a Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. Annual Book of ASTM Standards. Volume 4.02 Concrete and Aggregates. American Society for Testing and Materials, West Conshohocken, PA.

Benazzouk A, Douzane O, Mezreb K, Quéneudec M. 2006. Physico-mechanical Properties of Aerated Cement Composites Containing Shredded Rubber Waste. Cement & Concrete Composites. 28(7):650–657.

Brown RC, Dykstra J. 1995. Systematic Errors in the Use of Loss-on-Ignition to Measure Unburned Carbon in Fly Ash. Fuel. 74(4):570-574.

Bruere G. 1955. Air Entrainment in Cement and Silica Paste. Journal of the American Concrete Institute. 26(9):905-919.

Davis R, Carlson RW, Kelly JW, Davis HE. 1937. Properties of Cements and Concretes Containing Fly Ash. Journal of the American Concrete Institute. 33(5):577-612.

Dodson V. 1990. Concrete Admixtures. Van Nostrand Rienhold: New York, New York. p. 137-162.

Du L, Folliard K. 2005. Mechanisms of Air Entrainment in Concrete. Cement and Concrete Research. 35(8):1463-1471.

FHWA - Fly Ash. [Internet]. 2011. [cited: January 16, 2012]. Available from http://www.fhwa.dot.gov/infrastructure/materialsgrp/flyash.htm

Hachmann L, Burnett A, Gao Y, Hurt RH, Suurburg EM. 1998. Surfactant Adsorptivity of Solid Products from Pulverized Coal Combustion Under Controlled Conditions. Twenty-Seventh Symposium (International) on Combustion: The Combustion Institute. 27(2):2965–2971.

Harris, NJ. 2007. Evaluating the Influence of Fly Ash on Air Entrained Concrete. Dissertation, Cornell University, Ithaca, New York.

Harris NJ, Hover KC, Folliard KJ, Ley MT. 2008. The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part I-Evaluation of the State of Practice. Journal of ASTM International, On-line. 5(7):1-15.

Harris NJ, Hover KC, Folliard KJ, Ley MT. 2008a. The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part II-Development of a Standard Test Method: Apparatus and Procedure. Journal of ASTM International, On-line. On-line. 5(7):1-15.

Harris NJ, Hover KC, Folliard KJ, Ley MT. 2008b. The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part III-Development of a Standard Test Method: Proportions of Materials. Journal of ASTM International, On-line. 5(7):1-11.

Hewlett PC. 2004. Lea's Chemistry of Cement and Concrete, 4th ed. Oxford: Elsevier, Buuerworth-Heinemann. p. 32.

Hill R, Majors R. 2001. Fly Ash, Loss on Ignition, and Air Entrainment in Concrete A Subject Revisited. Proceedings: 14th International Symposium on Management and Use of Coal Combustion Products (CCPs). Bob Rathbone Center for Applied Energy Research, University of Kentucky, Lexington Kentucky. 1(34):1-19.

Külaots I, Hsu A, Hurt RH, Suuberg EM. 2003. Adsorption of Surfactants on Unburned Carbon in Fly Ash and Development of a Standardized Foam Index Test. Cement and Concrete Research. 33(12):2091 - 2099.

Külaots I, Hurt RH, Suuberg EM. 2004. Size Distribution of Unburned Carbon in Coal Fly Ash and its Implications. Fuel. 83(2):223-230.

Pedersen KH, Jensen AD, Skjøth-Rasmussen MS, Dam-Johansen K. 2008. A Review of the Interference of Carbon Containing Fly Ash with Air Entrainment in Concrete. Progress in Energy and Combustion Science. 34(2):135-154.

Sutter LL, Hooton RD, Schlorholtz S. 2013. NCHRP Project 18-13: Specifications and Protocols for Acceptance Tests of Fly Ash Used in Highway Concrete. National Cooperative Highway Research Program of the Transportation Research Board of The National Academies. Completed by the Michigan Tech Transportation Institute at Michigan Technological University (MTU), project final report under review.

UND EERC - Coal Ash Research: Historical Timeline. [Internet]. (n.d.). [cited: January 16, 2012]. Available from http://www.undeerc.org/carrc/html/HistoricalTimeline.html

2. Characterization of Coal Fly Ash by the Absolute Foam Index[1]

2.1 Abstract

The absolute foam index test was used to characterize fly ash samples having loss on ignition (LOI) values that ranged from 0.17 to 23.3 %wt. The absolute foam index characterized the fly ash samples by absolute volume of AEA, defined as the amount of undiluted AEA solution added to obtain a 15-minute endpoint signified by a 15-second metastable foam. Results were compared from several foam index test time trials that used different initial test concentrations to reach termination at selected times. Based on the coefficient of variation (CV), a 15-minute endpoint, with limits of 12 to 18 minutes was chosen. Various initial test concentrations were used to accomplish consistent contact times and concentration gradients for the 15-minute test endpoint for the fly ash samples.

2.2 Introduction

Numerous foam index test procedures for characterizing fly ash samples have been published with slight differences in common test variables. Although versions of the test are currently used by the concrete industry, no standard test method has been adopted, leading to differences in test variables such as concentration of air-entraining admixture (AEA) solution, cycle time, and time of metastable foam.

In this study, the absolute foam index test was used to characterize 15 fly ash samples with loss on ignition (LOI) values that ranged from 0.17 to 23.3 wt.%. The absolute foam index characterized the fly ash samples by absolute volume of AEA, defined as the amount of undiluted AEA solution added to obtain a 15-minute endpoint signified by 15-second metastable foam. The 15-second metastable foam at 15 minutes represented the

[1] The information contained in this chapter is currently being reformatted for publication in a peer reviewed journal.

aqueous phase AEA concentration in the slurry solution. The specified time of 15 minutes was constant across all tests for all 15 fly ash samples and was accomplished by varying the initial test solution concentration.

In the foam index test, AEA additions occur incrementally over a timed cycle. The total analysis time, associated with these cumulative incremental additions, affects the AEA adsorption by fly ash throughout the test. Step times were sufficiently defined by previously reported test procedures (Harris et al. 2008, Külaots et al. 2003, Baltrus et al. 2001, Dodson 1990, Dodson et al. 2005, FHWA 2003, FHWA 2006, Freeman et al. 1997, Gebler et al. 1983, Grace Construction Products 2006, Gurupira et al. 2005, Külaots et al. 2004, Meininger 1981, Separation Technologies, Inc. 2000, Separation Technologies, Inc. 2006, Zacarias 2000) but the total test time had not been considered. In this research, the significance of the total test time was addressed, and a total test time of 15 minutes was recommended based on the reproducibility of the test results.

The Harris et al. (2008) and Külaots et al. (2003) procedures were chosen over 13 other foam index test procedures (Baltrus et al. 2001, Dodson 1990, Dodson et al. 2005, FHWA 2003, FHWA 2006, Freeman et al. 1997, Gebler et al. 1983, Grace Construction Products 2006, Gurupira et al. 2005, Külaots et al. 2004, Meininger 1981, Separation Technologies, Inc. 2000, Separation Technologies, Inc. 2006, Zacarias 2000) as the basis for the absolute foam index test established in this study. The procedure recommended by Harris et al. (2008) was found to be the most reproducible procedure as it offered the lowest coefficient of variation (CV) among tests compared. The Külaots et al. (2003) test was chosen for evaluation because it allowed examination of a 10 vol.% AEA concentration versus a 5 vol.% concentration (2003, Harris et al. 2008), as specified by the other tests. The Harris et al. test was used to evaluate reproducibility when comparing manual versus automated agitation. Both the Harris et al. and Külaots et al. tests were used to evaluate the effects of AEA solution strength differences on different fly ash samples.

2.3 Materials and Methods

2.3.1 Materials

The materials consisted of 15 fly ash samples, one ASTM C150 Type I/II cement, distilled water, and two AEAs, as shown in Table 2.1. The 15 fly ash samples had a wide range of loss on ignition (LOI) values. LOI is a measure of the total carbon content by loss of mass at 750°F (ASTM 2011). These samples included two ASTM C618 Class C and 13 Class F fly ash samples.

Table 2.1

Fly ash and cement.

Fly Ash ID	Fly Ash Class	LOI (wt.%)
FA-8	F	0.17
FA-20	C	0.39
FA-1	F	0.87
FA-33	C	1.22
FA-10	F	1.26
FA-15	F	1.43
FA-7	F	2.25
FA-40	F	3.35
FA-32	F	6.06
FA-100 (blend)	F	10.37
FA-39	F	10.49
FA-101 (blend)	F	14.68
FA-102 (blend)	F	18.99
FA-36	F	21.34
FA-31	F	23.30
Type I/II portland cement		1.37

The AEAs used are common to the concrete industry. AEA-A was a vinsol resin and AEA-B was an alpha olefin sulfonate.

2.3.2 Foam Index Test Method

The foam index test involved adding a known volume of a dilute aqueous AEA solution to a slurry of fly ash, cement, and water. The slurry was then agitated for a period of time specified by the procedure, after which the slurry surface was visually monitored for a metastable foam. If the foam was not stable after one cycle (i.e. addition of the AEA, agitation, and observation), then additional cycles continued with AEA incrementally added until a metastable foam formed. The metastable foam was subjectively defined by the test performer but in general was defined as the foam that covered the entire surface of the slurry in the test container, and persisted for the prescribed observation time without dissipating (Harris et al. 2008, Külaots et al. 2003, Dodson 1990).

2.3.3 Harris et al. and Külaots et al. Foam Index Test Methods

The Harris et al. and Külaots et al. test procedures were performed to examine reproducibility and solution strength effects. Using FA-33, AEA-A, and portland cement, four sets of seven tests were performed following the Harris et al. procedure with modifications to include automatic agitation. For the automatic agitation tests, the Harris et al. procedure was modified for use of the Wrist-Action® laboratory shaker (WAS) manufactured by Burrell (Pittsburg, PA). The WAS motion was similar to a human hand shaking a bottle, but it ensured uniform agitation. The test statistic used to compare manual versus automatic agitation results was the coefficient of variation (CV) for each set of tests.

The Külaots et al. procedure was also modified for use of the WAS to examine the effects of AEA solution strength compared to those used in the Harris et al. procedure. The AEA concentration specified in the Külaots et al. procedure was 10 vol.% (2003), compared to

5 vol.% used in the Harris et al. procedure (2008). Sixteen sets of four Harris et al. (2008) procedure and Külaots et al. (2003) procedure foam index tests were performed with fly ash FA-33, FA-31, FA-32, portland cement, and AEA-A and AEA-B, and the results of each set of seven were averaged to compare Harris et al. to Külaots et al.

The Harris et al. (2008) procedure was modified slightly to accommodate the WAS. An AEA solution with 5 vol.% concentration was used (Harris et al. 2008). Harris et al. tested many containers and specified 'a container with a tight fitting cap' (2008). For tests in this study, a 200 ml plastic bottle with a tight-fitting cap was used, with 25 ml distilled water, 2.0 g of fly ash, and 8.0 g of cement combined (Harris et al. 2008). The container was secured in the WAS and agitated for 30 s. The cap was opened and a single drop (0.2 ml) of AEA solution was added (Harris et al. 2008). The container was closed and agitated with the WAS for another 10 s. The container was then opened and left undisturbed, and the air-slurry interface was observed for foam (Harris et al. 2008). If no foam was observed or foam was observed for less than 15 s, another 0.2 ml drop of AEA solution was added (Harris et al. 2008). The moment the technician noticed the foam was stable for less than 15 s; another drop was added, signifying the beginning of another cycle. Since the Harris et al. procedure did not specify a definite total cycle time; cycles were repeated until a metastable foam remained for 15 s. The total volume of AEA solution (Harris et al. 2008) and the total time to achieve a metastable foam were recorded.

The Külaots et al. (2003) procedure was also modified slightly to accommodate the WAS. The Külaots et al. and Harris et al. procedures are similar. The Külaots et al. procedure also does not specify a definite total cycle time. The differences that Külaots et al. specifies an AEA solution with 10 vol.% concentration, a 70 ml 40 mm diameter cylindrical jar, initial agitation for 1 min, and 15 s agitation after drop addition (2003). The foam index in the Külaots et al. procedure was recorded as the volume obtained by subtracting the blank test result from the test performed with the fly ash (2003). Külaots et al. recommends performing all combinations twice (2003).

2.3.4 Absolute Foam Index Test

Seven tests were performed with four different AEA concentrations using FA-32 (a fly ash with 6.06% LOI) to achieve target termination times of 5, 15, 25, and 30 minutes using the WAS. The CV was determined for each set of seven absolute volumes that resulted. The target test time that corresponded with the lowest CV was chosen as the target test time.

The modified Harris et al. procedure (2008) and various initial AEA test solution concentrations (rather than the 5 vol.% concentration as specified) were used on a trial-and-error basis to determine the absolute volume of AEA (ml) needed for test termination for each of the 15 fly ash samples. The absolute volume of AEA was calculated for each fly ash sample as:

$$\text{Absolute Volume AEA (ml of stock)} = N_D \; x \; V_D \; x \; C_S \tag{2.1}$$

where:

N_D = the number of drops

V_D = the volume of each drop, ml (0.2 ml)

C_S = initial test solution concentration (ml of stock/ml of solution, expressed as decimal)

Foam index tests were performed using 15 fly ash samples ranging in LOI % from 0.39% to 23.30% and AEA-A. Fifteen tests were performed with each fly ash sample until an amount of AEA solution maintained a 15-second metastable foam in the target test time. An additional repetition using the same fly ash sample and initial AEA test solution concentration was performed. Results from the two test repetitions were averaged and reported as the absolute foam index of the sample.

2.4 Results and Discussion

2.4.1 Harris et al. and Külaots et al.: Standard Agitation, Concentration Effects

A summary of results that achieved metastable foam from the four sets of Harris et al. procedure (2008) foam index tests, with modifications for automatic agitation, using materials FA-33 (1.22% LOI %), AEA-A, and portland cement, are shown in Table 2.2.

Table 2.2

Harris et al. (Harris et al. 2008) results in absolute volume of AEA-A (ml) with and without the Wrist-Action® Shaker.

Repetition	Manual		Wrist-Action® Shaker	
	Test 1	Test 2	Test 3	Test 4
1	0.0059	0.0050	0.0050	0.0055
2	0.0069	0.0040	0.0050	0.0065
3	0.0049	0.0050	0.0050	0.0055
4	0.0059	0.0040	0.0050	0.0065
5	0.0049	0.0050	0.0060	0.0070
6	0.0049	0.0050	0.0060	0.0065
7	0.0049	0.0050	0.0050	0.0065
Average	0.0055	0.0047	0.0053	0.0062
Min	0.0049	0.0040	0.0050	0.0055
Max	0.0069	0.0050	0.0060	0.0070
Standard Dev.	0.0008	0.0005	0.0005	0.0006
CV (%)	14.1	10.4	8.6	9.6

Reproducibility was expressed in terms of the CV (%) of the measured AEA required to obtain a metastable foam. Based on these results, the tests performed with the WAS had increased precision. Standard agitation through WAS use resulted in lower overall CV than manual tests. However, the CV values in Table 2.2 showed a single operator could perform tests and arrive at results that are likely acceptable depending on the precision desired.

A summary of average results from the eight sets of Harris et al. (2008) procedure and Külaots et al. (2003) procedure foam index tests, with modifications for automatic agitation, using materials FA-31 and FA-33, portland cement and AEA-A and AEA-B are shown in Table 2.3. Since Külaots et al. specified a 10 vol.% AEA concentration (2003) and Harris et al. specified a 5 vol.% concentration (2008), the results were reduced from average total volume of AEA solution to absolute volume of AEA for even comparison. Standard deviation for each test set is also reported.

Table 2.3

Average absolute volume of AEA-A (ml) (four tests for each combination) required for a metastable foam and standard deviation.

AEA	Test	Class C 1.22% LOI FA-33		Class F 23.3% LOI FA-31		Class F 6.3% LOI FA-32		portland cement	
		Avg abs vol (ml)	Standard deviation	Avg abs vol (ml)	Standard deviation	Avg abs vol (ml)	Standard deviation	Avg abs vol (ml)	Standard deviation
AEA-A	Külaots et al.	0.004	0.0010	0.163	0.0084	0.014	0.0000	0.006	0.0008
	Harris et al.	0.009	0.0010	0.151	0.0067	0.023	0.0026	0.005	0.0008
AEA-B	Külaots et al.	0.013	0.0011	0.167	0.0089	0.030	0.0010	0.013	0.0010
	Harris et al.	0.019	0.0011	0.144	0.0113	0.032	0.0015	0.018	0.0015

The Külaots et al. (2003) procedure resulted in the same absolute volume for the portland cement only and Class C fly ash (FA-33) tests performed with AEA-B. This indicated a solution concentration with high resolution was not suitable for detecting differences between low LOI content materials. In general, tests with the same cementitious material and AEA did not result in the same absolute volumes for tests with Külaots et al. and Harris et al. procedures as shown in Table 2.3. The different concentrations produced differences in resolution in the drops causing absolute volume differences. When an additional drop was needed to achieve a 15-second metastable foam in a Külaots et al. test, twice the amount of AEA was added as compared to an additional drop in a Harris et al. test.

Since the Harris et al. concentration is half that of Külaots et al., it is expected that the number of drops to metastable foam would be double. However, the number of drops for the Harris et al. tests were generally more than twice the amount needed for Külaots et al. tests as shown in Table 2.4. The indicated that difference in drop resolution affected absolute volume differences.

Table 2.4

Average number of drops required for a metastable foam.

AEA	Test	Class C 1.22% LOI FA-33	Class F 23.3% LOI FA-31	Class F 6.3% LOI FA-32	portland cement
AEA-A	Külaots et al.	2.3	81.3	7.0	2.9
	Harris et al.	4.7	150.6	22.5	5.6
AEA-B	Külaots et al.	6.4	81.7	16.5	7.3
	Harris et al.	19.1	144.1	32.5	18.2

It is also possible that higher concentrations could cause diffusion and reaction to be faster, so less volume of AEA was needed to reach metastable foam. This was suggested by comparison of absolute volume results for both the Külaots et al. and Harris et al. tests for the low (LOI) materials in Table 2.3.

Times required for 15-second metastable foam for the Harris et al. (2008) and Külaots et al. (2003) procedure are shown in Table 2.5. Overall, times required to achieve a 15-second metastable foam for tests performed with Külaots et al. (2003) procedure were less than those with the Harris et al. (2008) procedure, which was expected given the concentration differences. Only a time of approximately 4 minutes was required to reach the endpoint for either portland cement only or Class C fly ash (FA-33) tests performed with AEA-A.

Table 2.5

Foam index test results: total test times shown in minutes

AEA	Test	FA-ZE Class F 23.3% LOI (min)	FA-ZG Class C 1.22% LOI (min)	portland cement (min)
AEA-A	Külaots et al.	53.0	4.0	3.0
	Harris et al.	64.0	4.0	4.0
AEA-B	Külaots et al.	44.0	5.5	5.0
	Harris et al.	92.0	10.0	10.0

Higher AEA concentrations, such as the 10 vol.% specified by Külaots et al., resulted in shorter test times. However, test times for both procedures with high LOI fly ash were close to or over an hour. This indicated that higher concentrations would be more suitable for testing high adsorption fly ash.

A standard test time, practical for all fly ash-AEA combinations, is desired where the contact time between the AEA solution and the fly ash were as similar as possible was desired. A uniform contact time would reduce the variability of adsorbate concentration gradient and allow the fly ash to be characterized solely by the absolute volume of AEA necessary to produce the 15-second metastable foam. Tests were conducted with five test times between 5 and 30 minutes for a standard test time.

2.4.2 Absolute Foam Index Test

Seven foam index test repetitions using four different concentrations of AEA-A were performed on FA-32, a 6.06% LOI fly ash to examine test time alternatives. The CV of absolute volume of AEA-A was examined at a range of AEA concentrations as shown in Table 2.6.

Table 2.6

Foam index tests results for FA-32 in CV% from ml of AEA-A, n=7 for each value

AEA Concentration	12 vol.%	8 vol.%	4 vol.%	3 vol.%	2 vol.%
Mean Test Time (min)	5.90	10.00	15.04	24.49	31.76
CV % of ml of AEA	10.39	7.57	4.61	6.30	7.06
Average # of Drops	7.6	22.1	27.6	31.6	60.6

A 4 vol.% AEA concentration and 15-minute endpoint, with limits of 12 to 18 minutes, was chosen as the test duration because this time period produced the most consistent test results, as shown by the lowest CV %. The 15-minute time period allowed the fly ash sample to be exposed to the optimal drop resolution and sensitivity. In contrast, the 6-minute test used fewer drops of a higher concentration (low resolution) and the 25-minute and 32-minute tests used more drops of concentrations that were too dilute (low sensitivity).

Results from the 28 replicate absolute foam index tests that terminated at the 15-minute endpoint for 14 fly ash samples are shown in Table 2.**7**. For each fly ash sample, the unique concentration and time to 15-second metastable foam are reported. A 15 minute test time provided adequate resolution for both low and high carbon fly ash correlating with LOI for R^2 of 0.94 as shown Figure 2.1.

Table 2.7

Absolute foam index test results; n=2 for each value

Fly Ash ID	Fly Ash Class	LOI	Test Concentration AEA-A (vol.%)	Time to metastable foam (min)	Absolute Volume AEA-A (ml)	Absolute Volume AEA-A per g FA (ml/g)
FA-8	F	0.17	2	11.84	0.01	0.005
FA-20	C	0.39	2	12.48	0.0076	0.0038
FA-1	F	0.87	2	17.60	0.0154	0.0077
FA-10	F	1.26	2	14.83	0.011	0.0055
FA-15	F	1.43	4	15.33	0.0292	0.0146
FA-7	F	2.25	3	12.17	0.0123	0.0062
FA-40	F	3.35	5	14.08	0.0285	0.0143
FA-32	F	6.06	4	13.13	0.0212	0.0106
FA-100	F	10.37	6	14.55	0.0414	0.0207
FA-39	F	10.49	6	13.98	0.0468	0.0234
FA-101	F	14.68	10	13.80	0.064	0.032
FA-102	F	18.99	15	12.24	0.075	0.0375
FA-36	F	21.34	15	14.08	0.0945	0.0473
FA-31	F	23.30	16	14.25	0.1184	0.0592

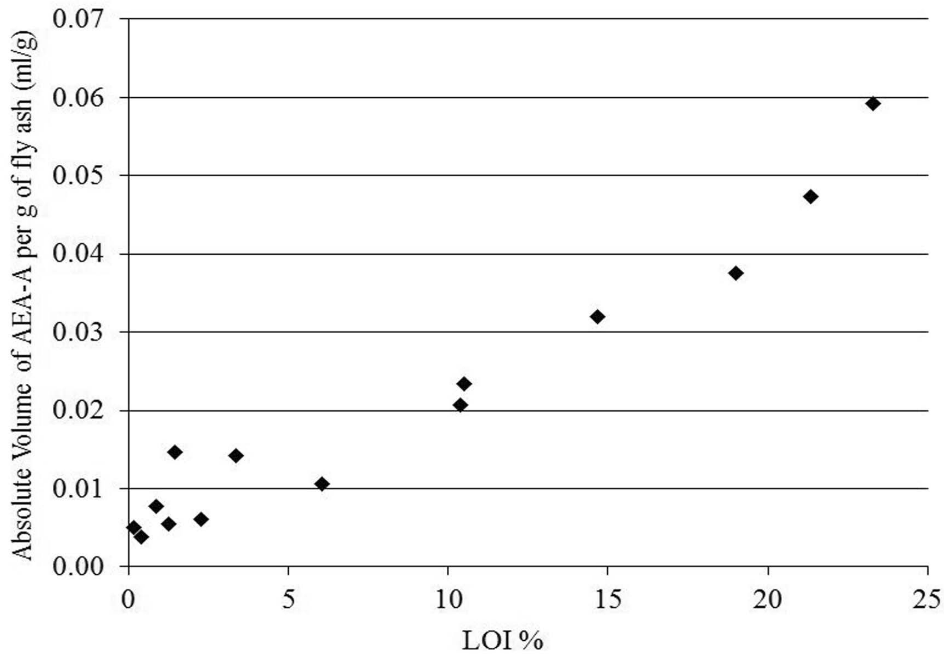

Figure 2.1 The AEA-A absolute foam index per g of fly ash (ml/g) versus 14 fly ash samples with LOI ranging from 0.39% to 23.30%

The absolute foam index increased consistency for fly ash greater than 5% LOI while more variability in the correlation was apparent where carbon content was less than 5% LOI. At an LOI less than 5%, LOI was not as representative of adsorption capacity of fly ash, possibly due to inorganic burnout in the LOI test (Dodson 2005, Brown et al. 1995, Pedersen et al. 2008). LOI test results may error up to 75% because mass loss in the LOI test includes not only the loss due to carbon combustion but also mass loss of portlandite, carbonate, bound water, and gains from iron and sulfur oxidation (Dodson 2005, Brown et al. 1995). Additional research may be able to refine variability in the foam index-LOI correlations for fly ash with less than 5% LOI.

2.5 Conclusion

A fixed test time was necessary for a constant contact time and concentration gradient between the cementitous materials and AEA in the slurry solution. A 15-minute duration forced the test into a number of cycles where AEA drops with sensitivity compatible to the fly ash allowed diffusion and reaction to be consistent throughout all tests. This allowed both low and high carbon fly ash to be characterized uniquely. Results obtained using automated agitation were more precise than results obtained using manual agitation; therefore, automated agitation is recommended.

The 5 vol.% AEA test solution concentration procedure specified by Harris et al. (2008) and the 10 vol.% test solution concentration specified by Külaots et al. (2003) were not applicable to all fly ash. The test solution concentrations of 5 vol.% and 10 vol.% specified by the Harris et al. (2008) and Külaots et al. (2003) procedures resulted in tests where a 15-second metastable foam was not produced for high-carbon fly ash in less than an hour as well as tests where differences in low LOI cementitious materials could not be detected.

Long test times and the inability to characterize different low LOI cementitious materials using the same solution concentrations prompted examination of different test solution concentrations for various fly ash samples. A constant contact time and concentration gradient at a 15-minute endpoint, signified by 15-second metastable foam for all fly ash samples, was specified and results determined by use of unique initial concentrations. The absolute volume of AEA characterized this wide range of fly ash at that particular endpoint.

Nine different AEA concentrations were used to characterize the ash sources reported here. A thorough review of the data that was collected from the-trial-and-error iterations to find those initial concentrations that led to the 15-minute endpoint for each fly ash and sample formulation of a procedure to determine initial concentrations should be completed in future work.

The absolute foam index successfully characterized 14 fly ash samples, with a strong correlation with LOI in fly ash with more than 5% LOI. However, significant variability was observed in fly ash with less than 5% LOI. This was in agreement with past studies that stated that LOI ranged in accuracy and may not always be a true measure of carbon content. To determine if absolute foam index results are an indicator of fly ash carbon adsorption equilibrium they should be compared in future work.

2.7 References

ASTM. 2011. ASTM C311-11a Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete. Annual Book of ASTM Standards. Volume 4.02 Concrete and Aggregates. American Society for Testing and Materials, West Conshohocken, PA.

Baltrus JP, LaCount RB. 2001. Measurements of Adsorption of Air-Entraining Admixture on Fly Ash in Concrete and Cement. Cement and Concrete Research. 31(5): 819-824.

Brown R.C.; Dykstra J. 1995. Systematic Errors in the Use of Loss-on-Ignition to Measure Unburned Carbon in Fly Ash. Fuel. 74(4):570-574.

Dodson V. 1990. Concrete Admixtures. Van Nostrand Rienhold: New York, New York. p. 137-162.

Dodson V, LaCount RB, Kern DG. 2005. Economical Treatment of High Carbon Fly Ash to Produce a Low Foam Index Product with Carbon Content Retained. Waynesburg College, Waynesburg, PA. Report. Available from: http://wvwri.nrcce.wvu.edu/programs/CBRC/reports/99-EC-E04.pdf

FHWA - Fly Ash Facts for Engineers. 2003. [Internet]. Report No. FHWA-IF-03-019. [cited: February 10, 2010]. Available from http://www.fhwa.dot.gov/Pavement/recycling/fafacts.pdf

FHWA. 2006. Identifying Incompatible Combinations of Concrete Materials: Volume II - Test Protocol. Publication No. FHWA-HRT-06-080. US DOT, McLean, VA

Freeman E, Gao YM, Hurt RH, Suuberg EM. 1997. Interactions of Carbon-containing Fly Ash with Commercial Air-entraining Admixtures for Concrete. Fuel, Vol. 76, No. 8, 1997, pp. 761-765.

Gebler S, Klieger P. 1983. Effect of Fly Ash on the Air-Void Stability of Concrete. Proc., 1st International Conference on the Use of Fly Ash, Silica Fume, Slag and Other Mineral By-Products in Concrete, Montebello, Quebec, Canada. 103-142.

Grace Construction Products - The Foam Index Test: A Rapid Indicator of Relative AEA Demand. TB-0202. [Internet]. 2006. Grace Construction Products, Columbia, Md. [cited: May 9, 2011]. Available from http://www.na.graceconstruction.com/custom/concrete/downloads/TB_0202.pdf

Gurupira TZ, Ochsenbein, M. P.; Stencel, J. M.; Martinus; F. 2005. Development of an Automated Foam Index Test. 2005 World of Coal Ash Conference. Proceedings. Lexington, KY. Available from http://www.flyash.info/2005/13gur.pdf

Harris NJ, Hover KC, Folliard KJ, Ley MT. 2008. The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part II-Development of a Standard Test Method: Apparatus and Procedure. Journal of ASTM International, On-line. On-line. 5(7):1-15.

Külaots I, Hsu A, Hurt RH, Suuberg EM. 2003. Adsorption of Surfactants on Unburned Carbon in Fly Ash and Development of a Standardized Foam Index Test. Cement and Concrete Research. 33(12):2091-2099.

Külaots I, Hurt RH, Suuberg EM. 2004. Size Distribution of Unburned Carbon in Coal Fly Ash and its Implications. Fuel. 83(2):223-230.

Meininger RC. 1981. Use of Fly Ash in Concrete-Report of Recent NSGA-NRMCA Research Laboratory Studies-Series J 153. Technical Information Letter No. 381. National Ready-Mixed Concrete Association, Silver Spring, Md.

Pedersen KH, Jensen AD, Skjøth-Rasmussen MS, Dam-Johansen K. 2008. A Review of the Interference of Carbon Containing Fly Ash with Air Entrainment in Concrete. Progress in Energy and Combustion Science. 34(2):135-154.

Separation Technologies, Inc. 2000. Foam Index Procedure. Unpublished Test Procedure, Needham, Mass.

Separation Technologies, Inc. 2006. Modified Foam Index Procedure for Class F Fly Ashes. Unpublished Test Procedure, Needham, Mass.

Stencel JM, Song H, Cangialosi F. 2009. Automated Foam Index Test: Quantifying Air Entraining Agent Addition and Interactions with Fly Ash-Cement Admixtures. Cement and Concrete Research. 39(4):362-370.

Zacarias P. 2000. Modified Foam Index For Class C Fly Ashes. Unpublished Test Procedure. Lafarge Canada Inc. Montreal, Quebec, Canada.

3. A Standard Test Procedure for Absolute Foam Index Test for Coal Fly Ash[2]

3.1 Abstract

This study defined a set of four standard concentrations for the absolute foam index test by regression analyses and a procedure simplifying the test process. The set of standard concentrations for the absolute foam index test was determined by analyzing experimental results of 80 tests on coal fly ashes with loss on ignition (LOI) values ranging from 0.39 to 23.3 wt.%. A regression analysis informed selection of four concentrations (2, 6, 10, and 15 vol.% AEA) that are expected to accommodate fly ashes with 0.39 to 23.3 wt.% LOI, depending on the AEA type. Higher AEA concentrations should be used for high-LOI fly ash when necessary. A procedure developed using these standard concentrations is expected to require only 1-3 trials to meet specified endpoint criteria for most fly ashes.

3.2 Introduction

The absolute foam index test used sixteen initial air-entraining admixture (AEA) concentrations over a lengthy iterative approach to characterize 15 fly ash samples (AEA) in a previous work. This study defined a set of four standard concentrations for the absolute foam index test by regression analyses and a procedure simplifying the test process.

The absolute foam index test originated from the review of 15 published procedures (Baltrus et al. 2001, Dodson 1990, Dodson et al. 2005, FHWA 2003, FHWA 2006, Freeman et al. 1997, Gebler et al. 1983, Grace Construction Products 2006, Gurupira et

[2] The information contained in this chapter is currently being reformatted for publication in a peer reviewed journal.

al. 2005, Harris et al. 2008, Külaots et al. 2003, Külaots et al. 2004, Meininger 1981, Separation Technologies, Inc. 2000, Separation Technologies, Inc. 2006, Zacarias 2000), and from these the Harris et al. procedure (2008) was modified for use of the Wrist-Action® laboratory shaker (WAS) and test limits of 12 to 18 minutes were specified. The Harris et al. (2008) agitation times were adopted, but the specified 5 vol.% concentration was replaced with various initial AEA concentrations determined by a lengthy iterative process.

In this study, 80 test sets (of two tests each) were performed on 15 fly ash samples with loss on ignition (LOI) ranging from 0.39 to 23.3 wt.%, three cements and five AEAs of various types representing those used in industry. These test sets included 15 test sets from prior work and 65 additional test sets. Unique initial AEA concentrations, times to 15-second metastable foam, and absolute volume of AEA to metastable foam are reported for each fly ash sample tested. A regression analysis was performed to model the test data using the foam index test variables: initial solution concentration of AEA, the time to test termination, and absolute volume of AEA required to produce metastable foam.

The sixteen initial AEA concentrations were reduced to the set of initial concentrations that most frequently satisfied tests and then termination times were calculated using the regression equation. The set of most frequently used initial AEA concentrations that satisfy the regression equation are 2, 6, 10, and 15 vol. %. A procedure to simplify the trial and error process of selecting an initial AEA concentration was developed based on these results.

3.3 Materials and Methods

3.3.1 Materials

The materials consisted of 15 fly ash samples, two ASTM C150 Type I/II cements, one type I limestone cement (additional $CaCO_3$) with slightly elevated total alkalis (Na_2O +

$K_20 > 0.6$), distilled water, and five AEAs, as shown in Table 3.1 and Table 3.2. The 15 fly ash samples ranged in loss on ignition (LOI) from 0.39 to 23.3 wt. %. LOI is a measure of the total carbon content by loss of mass at 750°F (ASTM 2011). These samples included two ASTM C618 Class C and 13 Class F fly ash samples. The five AEAs used are common to the concrete industry, and their chemical compositions are indicated in Table 3.2.

Table 3.1

Fly ash and cement.

Fly Ash ID	Fly Ash Class	LOI (wt.%)
FA-8	F	0.17
FA-20	C	0.39
FA-1	F	0.87
FA-33	C	1.22
FA-10	F	1.26
FA-15	F	1.43
FA-7	F	2.25
FA-40	F	3.35
FA-32	F	6.06
FA-100 (blend)	F	10.37
FA-39	F	10.49
FA-101 (blend)	F	14.68
FA-102 (blend)	F	18.99
FA-36	F	21.34
FA-ZE (31)	F	23.30
Type I/II (PC-1)		1.37
Type I/II (PC-2)		0.90
Type I (PC-3)		1.90

Table 3.2

AEAs and chemical information.

Name	Surfactant Type
AEA-A	Vinsol Resin
AEA-B	Alpha Olefin Sulfonate
AEA-C	Benzene Sulfonate
AEA-D	Resin/Rosin/Fatty Acid
AEA-E	Resin/Rosin/Fatty Acid

3.3.2 Absolute Foam Index Test

Eighty absolute foam index test sets were conducted with combinations of 15 fly ash samples, three cements, and various initial concentrations of five AEAs. Each test set consisted of a test and an additional repetition of the same fly ash-cement-initial AEA solution concentration or cement-initial AEA solution concentration. Results from the duplicates were averaged and reported as the absolute foam index of the sample.

A 200 ml, plastic bottle with a tight-fitting screw cap was used, where 25 ml distilled water, 2.0 g of fly ash, and 8.0 g of cement were combined (Harris et al. 2008). The container was secured in the WAS and agitated for 30 s. The cap was opened and a single drop (0.2 ml) of AEA solution was added (Harris et al. 2008) with a 20 μl pipette manufactured by Eppendorf (Stevenage, United Kingdom). The container was then closed and agitated with the WAS manufactured by Burrell (Pittsburg, PA) for 10 s. The container was opened and leaving the container undisturbed, the air-slurry interface was observed for foam (Harris et al. 2008). If no foam was observed, or foam existed for less than 15 s, a single 0.2 ml drop of AEA solution was added (Harris et al. 2008). The moment the technician noticed the foam was not metastable (less that 15 s), another drop was added, signifying the beginning of another cycle.

Cycles were repeated until a metastable foam remained for 15 s. The total volume of AEA solution (Harris et al. 2008) and the total time to a metastable foam were recorded. If the test required more than 18 minutes to achieve a metastable foam, another test was performed with a higher AEA concentration. Likewise, if the test resulted in a 15-second metastable foam in less than 12 minutes, another test was performed with a lower AEA concentration.

Upon termination, the absolute volume of AEA was calculated for each fly ash sample as:

$$\text{Absolute Volume AEA (ml of stock)} = N_D \; x \; V_D \; x \; C_S \tag{1}$$

where:
N_D = the number of drops
V_D = the volume of each drop, ml (0.2 ml)
C_S = initial solution concentration (ml of stock/ml of dilution)

3.3.3 Regression Analysis

In order to inform development of a standard test procedure, a multiple linear regression analysis was performed on the measured data from the 80 test sets to form a regression equation. In the foam index test the dependent variable was the absolute volume of AEA, or the required amount of AEA to produce the metastable foam. The independent variables were C_0, the initial concentration of AEA used to produce a metastable foam, and *t,* the time to test termination. The standard, linear regression equation format was used to develop the relationship that defined the measured data:

$$Absolute\ Volume\ of\ AEA\ (ml) = a\ C_0 + b\ t + d + \mathcal{E} \tag{2}$$

where a, b, and d are the calculated (predicted) regression coefficients and ε is the residual, or error term. The values of the coefficients were determined by minimizing the sum of the squared residuals.

Once the regression equation was determined using the measured data, an independent sensitivity analysis was performed using additional linear regression analyses that tested the sum of squared residuals to establish the degree to which these coefficients could vary. This tested the robustness of the relationship.

The initial concentrations used in the trial and error approach were examined for the most frequently used concentrations. The least frequently used initial concentrations were set to the next highest or lowest concentration used with a higher frequency. Using the modified concentration set, test times to termination were predicted using the model, Eq. 2, rearranged as follows:

$$t = (1/b)*(A - aC_o - d) \qquad (3)$$

where A = Absolute Volume of AEA (ml). The modified initial concentration was deemed acceptable if the calculated test time fell within the 12 to 18 minutes test endpoint limits.

3.4 Results and Discussion

3.4.1 Absolute Foam Index Test Results

Sixteen initial AEA solution concentrations, of 1-10, 12, 14-16, 20, and 25 vol.%, were used to complete the 80 absolute foam index test sets. Since the absolute volume of AEA for each fly ash sample was determined via an iterative trial and error approach, multiple tests were often conducted in order to produce 15-second metastable foam in times greater than 12 minutes and less than 18 minutes. A sample of these test results is shown in Table 3.3. The initial solution concentrations that were used to meet the 15-second metastable foam and 12 to 18 minute test termination requirements were documented.

Table 3.3

Sample absolute foam index test results. Bold indicates tests that met specified requirements.

Fly Ash / Cement ID	LOI %	Initial Concentration (vol.%) (AEA – E)	Time to metastable foam (min)	Average # of Drops	Absolute Volume AEA-E (ml)
FA-8	0.17	4	18.00	42	0.0336
FA-8	0.17	10	6.57	16	0.0320
FA-8	**0.17**	**6**	**15.57**	**38.5**	**0.0462**
FA-7	2.25	10	9.37	23	0.0460
FA-7	**2.25**	**8**	**14.3**	**34**	**0.0544**
FA-40	3.35	20	8.17	19	0.0760
FA-40	3.35	16	11.37	27	0.0864
FA-40	**3.35**	**10**	**16.27**	**42**	**0.084**
PC-1		7	18.00	41	0.0574
PC-1		**9**	**12.92**	**31**	**0.0558**

For example, a 20 vol.% concentration of AEA-E was used for the first test conducted with FA-40. This test terminated with a metastable foam lasting 15 seconds obtained in just over 8 minutes. Since the achievement of the metastable foam was desired in 12 to 18 minutes of test time, a new test was initiated with an initial concentration of 16 vol.%. This second test terminated with a 15 second metastable foam obtained in just less than 12 minutes. A third test was initiated using a 10 vol.% concentration, producing a 15 second metastable foam in just over 16 minutes. Absolute volumes of all tests shown for FA-40 were between 0.076 to 0.086 ml. Results similar to those described for FA-40 were also obtained for other fly ashes and cements, as shown in Table 3.3.

However, it should be noted that even though absolute volumes for tests that terminated in less than 12 minutes were close in range to tests conducted between 12 and 18 minutes, test variability, based on coefficient of variation (COV), was previously found to be lowest for tests terminating between 12 and 18 minutes.

3.4.2 Regression Analysis

A multiple linear regression equation was developed to relate measured absolute volumes (ml), initial solution concentrations (vol. %), and test termination times (min) from the 80 test sets. The regression analysis produced values for the regression coefficients *a*, *b*, and *d* of 0.0073, 0.0040, and -0.0586 respectively, as shown in Equation 4:

$$\text{Absolute Volume of AEA (ml)} = 0.0073\, C_0 + 0.0040\, t - 0.0586 \tag{4}$$

Using this equation, absolute volumes could be predicted for each initial concentration and test termination time. The predicted absolute volumes were plotted versus the experimental absolute volumes as shown in Figure 3.1, with an R^2 of 0.97 indicating that the regression equation provides an acceptable estimate of the actual data.

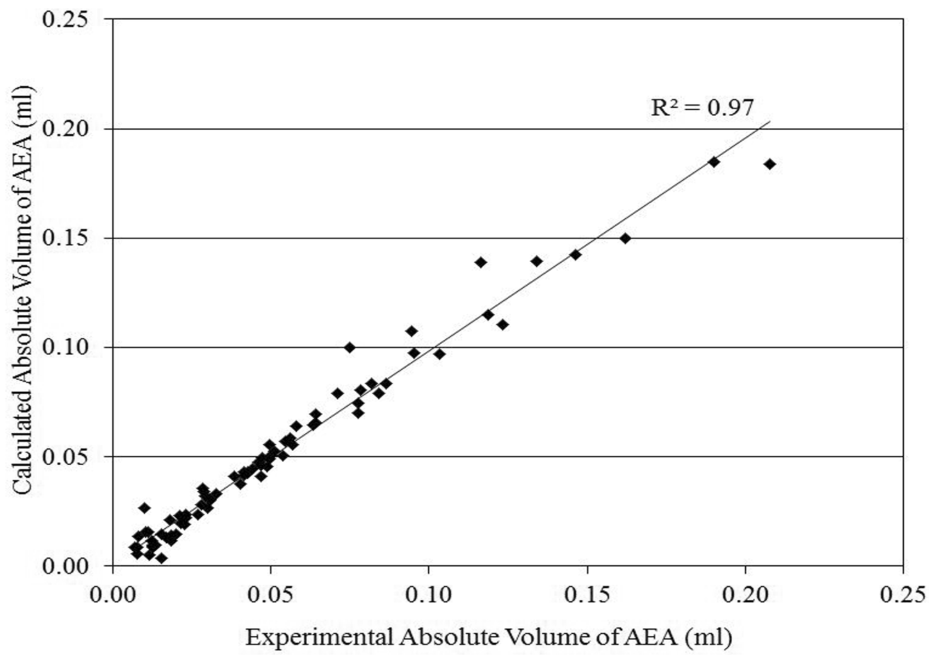

Figure 3.1 Calculated (predicted) absolute volumes of AEA versus the experimental (actual) absolute volumes of AEA.

The total sum of squared residuals from this regression model was 0.0036. A sensitivity analysis was performed with the constant *d* set to zero and the regression analysis repeated. This produced regression coefficients of *a* and *b* of 0.0072 and 0.000012, respectively, and resulted in an R^2 of 0.95 and a total sum of squared residuals of 0.0066. Thus, the sensitivity analysis produced only negligible changes in R^2 and the sum of squared residuals so equation 4 was deemed acceptable for use.

The initial concentrations were examined for the most frequently used. Initial concentrations were moved to the next highest or lowest most frequent concentration. The measured absolute volume and the modified initial concentration for each test were used in Equation 4 to calculate (predict) a test time for each of the 80 tests. If a predicted test time fell outside the 12 to 18 minute test endpoint range, the initial concentration was set to the next most frequent concentration (higher or lower), such that calculated test times fell within 12 to 18 minutes. The most frequent concentrations satisfying this test criterion were 2, 6, 10, and 15 vol. %, as shown in Figure 3.2.

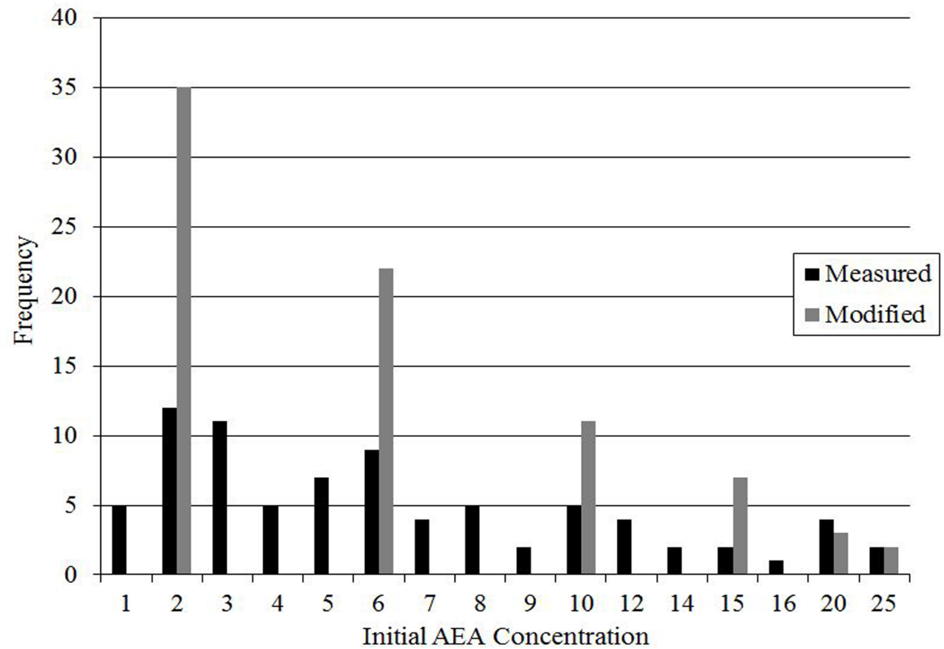

Figure 3.2 Frequency of measured and modified initial AEA concentrations.

With some high LOI fly ash it was necessary to use higher initial concentrations of AEA solution of 20 and 25 vol.% in order to meet the 12 to 18 minute test termination requirement.

The standard deviation of the set of measured test times was 1.52 min., and the standard deviation of calculated test times (with modified initial concentrations) was 1.92 min. Thus, modifying the initial concentrations within the specified 12 to 18 minute test limit is not expected to significantly affect the spread of the test times.

3.4.3 Absolute Foam Index Test Procedure

The absolute foam index test procedure as outlined in Figure 3.3 specifies use of the concentrations most frequently satisfying the endpoint criterion, specifically 2, 6, 10, and 15 vol.%. With use of these concentrations as specified in the procedure, a maximum of three absolute foam index tests with different initial concentrations will be required for the majority of fly ashes with between 0.39 to 23.3% LOI.

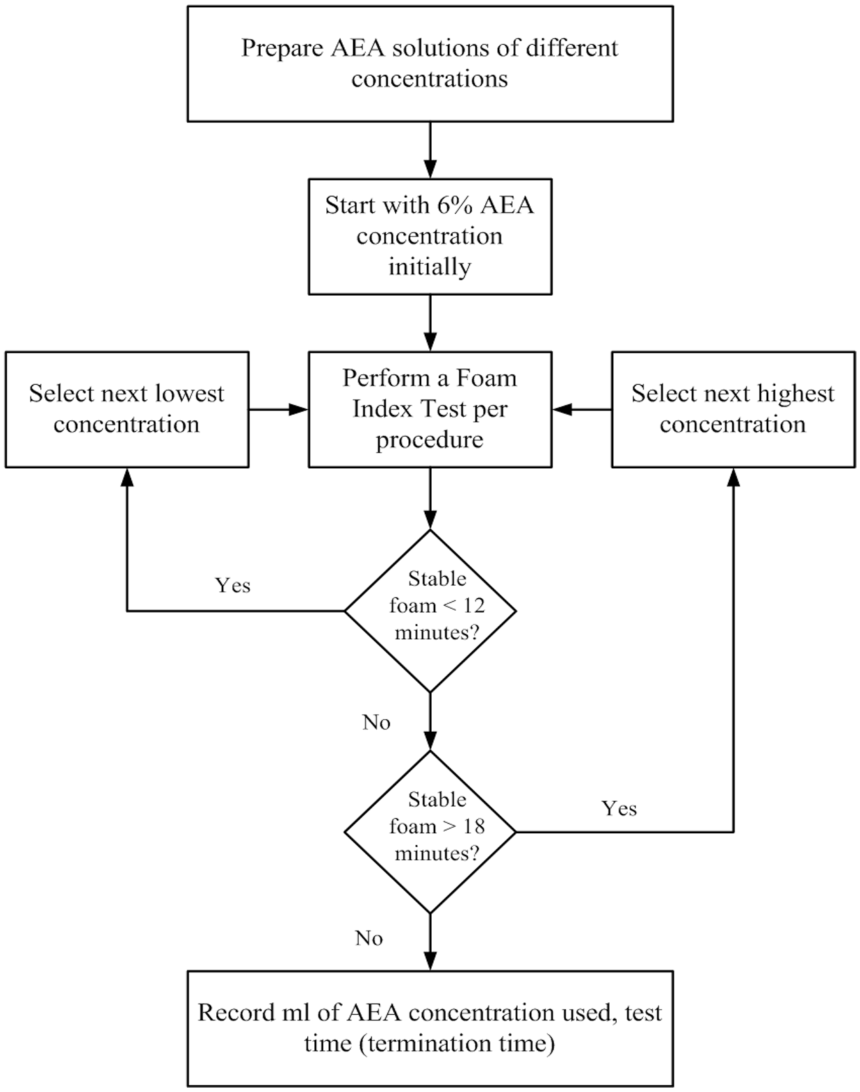

Figure 3.3 The absolute foam index test procedure outline.

The absolute foam index test procedure specifies that the first foam index test on a fly ash sample should be conducted with 6 vol.% AEA. If a 15-second metastable foam occurs in just less than 12 minutes, a second test should be conducted with the next lowest initial concentration, 2 vol.%. The test conducted with an initial concentration of 2 vol.% is expected to result in a 15-second metastable foam between 12 to 18 minutes. If a 15-second metastable foam occurs in over 18 minutes, the second test should be conducted with the next highest initial concentration, 10 vol.%. If this fails to produce a 15-second metastable foam in under 18 minutes, a third test should be conducted with the next highest initial concentration, 15 vol.%. In the instance that a 15 vol.% initial solution concentration cannot produce a 15-second metastable in under 18 minutes, an initial solution concentration greater than 15 vol.% should be used. When a 15-second metastable is achieved within the 12 to 18-minute endpoint window, the ml of solution used and test termination time should be recorded.

3.5 Conclusion

The absolute foam index test procedure was validated by performing the test with five AEAs, three cement types, and coal fly ash samples with LOI ranging from 0.25 to 23.3%. Each of the 80 tests was completed in a 12 to 18 minute time window.

A multiple regression analysis performed on the complete set of 80 test results guided selection of a set of four AEA concentrations that can be used to satisfy the termination criteria of a 15-second metastable foam within a 12 to 18 minute endpoint window for a vast majority of the fly ashes and cement types. The concentrations that most frequently satisfied the test set were 2, 6, 10, and 15 vol.% concentrations (with the exception of some high LOI fly ash). Using these concentrations with the proposed procedure is expected to reduce the complexity of the test by limiting the number of trials required for any fly ash sample, with exception of some high LOI fly ashes.

Five test sets that involved coal fly ash sources with high LOI values 10.37 and 10.69% did not satisfy the endpoint requirements when the initial concentration was set equal to 15 vol.%, while 23.3% LOI fly ash was satisfied with the 15 vol% initial concentration from the chosen test set. With some high LOI fly ash it may be necessary to use higher initial concentrations of AEA solution (20-25 vol.%) in order to meet the 12 to 18 minute test termination requirement. This indicates that LOI has questionable reliability as a measure of carbon content and carbon adsorption capacity. To determine whether foam index results are representative of carbon adsorption capacity, they should be compared to adsorption isotherms in future work.

3.6 References

ASTM. 2011. ASTM C311-11a Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete. Annual Book of ASTM Standards. Volume 4.02 Concrete and Aggregates. American Society for Testing and Materials, West Conshohocken, PA.

Baltrus JP, LaCount RB. 2001. Measurements of Adsorption of Air-Entraining Admixture on Fly Ash in Concrete and Cement. Cement and Concrete Research. 31(5): 819-824.

Dodson V. 1990. Concrete Admixtures. Van Nostrand Rienhold: New York, New York. p. 137-162.

Dodson V, LaCount RB, Kern DG. 2005. Economical Treatment of High Carbon Fly Ash to Produce a Low Foam Index Product with Carbon Content Retained. Waynesburg College, Waynesburg, PA. Report. Available from: http://wvwri.nrcce.wvu.edu/programs/CBRC/reports/99-EC-E04.pdf

FHWA - Fly Ash Facts for Engineers. 2003. [Internet]. Report No. FHWA-IF-03-019. [cited: February 10, 2010]. Available from http://www.fhwa.dot.gov/Pavement/recycling/fafacts.pdf

FHWA. 2006. Identifying Incompatible Combinations of Concrete Materials: Volume II - Test Protocol. Publication No. FHWA-HRT-06-080. US DOT, McLean, VA

Freeman E, Gao YM, Hurt RH, Suuberg EM. 1997. Interactions of Carbon-containing Fly Ash with Commercial Air-entraining Admixtures for Concrete. Fuel, Vol. 76, No. 8, 1997, pp. 761-765.

Gebler S, Klieger P. 1983. Effect of Fly Ash on the Air-Void Stability of Concrete. Proc., 1st International Conference on the Use of Fly Ash, Silica Fume, Slag and Other Mineral By-Products in Concrete, Montebello, Quebec, Canada. 103-142.

Grace Construction Products - The Foam Index Test: A Rapid Indicator of Relative AEA Demand. TB-0202. [Internet]. 2006. Grace Construction Products, Columbia, Md. [cited: May 9, 2011]. Available from http://www.na.graceconstruction.com/custom/concrete/downloads/TB_0202.pdf

Gurupira TZ, Ochsenbein, M. P.; Stencel, J. M.; Martinus; F. 2005. Development of an Automated Foam Index Test. 2005 World of Coal Ash Conference. Proceedings. Lexington, KY. Available from http://www.flyash.info/2005/13gur.pdf

Harris NJ, Hover KC, Folliard KJ, Ley MT. 2008. The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part II-Development of a Standard Test Method: Apparatus and Procedure. Journal of ASTM International, On-line. On-line. 5(7):1-15.

Külaots I, Hsu A, Hurt RH, Suuberg EM. 2003. Adsorption of Surfactants on Unburned Carbon in Fly Ash and Development of a Standardized Foam Index Test. Cement and Concrete Research. 33(12):2091-2099.

Külaots I, Hurt RH, Suuberg EM. 2004. Size Distribution of Unburned Carbon in Coal Fly Ash and its Implications. Fuel. 83(2):223-230.

Meininger RC. 1981. Use of Fly Ash in Concrete-Report of Recent NSGA-NRMCA Research Laboratory Studies-Series J 153. Technical Information Letter No. 381. National Ready-Mixed Concrete Association, Silver Spring, Md.

Separation Technologies, Inc. 2000. Foam Index Procedure. Unpublished Test Procedure, Needham, Mass.

Separation Technologies, Inc. 2006. Modified Foam Index Procedure for Class F Fly Ashes. Unpublished Test Procedure, Needham, Mass.

Stencel JM, Song H, Cangialosi F. 2009. Automated Foam Index Test: Quantifying Air Entraining Agent Addition and Interactions with Fly Ash-Cement Admixtures. Cement and Concrete Research. 39(4):362-370.

Zacarias P. 2000. Modified Foam Index For Class C Fly Ashes. Unpublished Test Procedure. Lafarge Canada Inc. Montreal, Quebec, Canada.

4. Foam Index Test Results Correlations to Equilibrium Isotherms & Examination of Mortar Air[3]

4.1 Abstract

Equilibrium isotherm equations obtained from direct isotherm tests were used to calculate the equilibrium concentrations and capacities of fly ash from 0.17 to 10.5% LOI. The results showed that the fly ash capacity calculated using the absolute foam index was much less than capacities obtained from isotherm tests that were conducted with higher initial concentrations. This indicated that the absolute foam index was not equilibrium. Rather, the test is dynamic where the time of the test played an important role in the results. Even though the absolute foam index was not an equilibrium condition, a correlation was made between the absolute foam index and adsorption isotherms for fly ash of 0.17 to 10.5% LOI.

Several batches of mortars were mixed for the same fly ash type increasing only the AEA concentration (dosage) in each subsequent batch. Mortar air test results for each batch showed for each increase in AEA concentration, air contents increased until a point where the next increase in AEA concentration resulted in no increase in air content. This was the maximum air content that could be achieved by the particular mortar system; the system reached its air capacity at the saturation limit. This concentration of AEA was compared to the adsorption isotherm capacity and critical micelle concentration (CMC) for the AEA.

[3] The information contained in this chapter is currently being reformatted for publication in a peer reviewed journal.

4.2 Introduction

The foam index test typically involves adding a specified amount of a dilute solution of AEA [the adsorbate] of a particular known concentration to a slurry of fly ash, cement, and water [where fly ash and cement are the sorbents]. After the addition, the slurry is agitated for a period of time specified by the procedure, and the slurry surface is then visually monitored for "stable foam." If the foam is not stable after one "cycle" (i.e. addition of the AEA, agitation, and observation), then additional cycles continue with AEA additions incrementally added until a metastable foam forms. Determination of the metastable foam is subjective. In general, a metastable foam is defined as one that covers the entire surface of the slurry in the test container, and persists for the prescribed observation time without dissipating. Recognizing a metastable foam can be time consuming and difficult for users, depending upon the ash type and AEA concentration used to complete the test. When a metastable foam exists for the specified time, the known number of AEA increments and the AEA concentration are used to calculate the total amount of AEA required to achieve a metastable foam. The total amount of AEA required to achieve a metastable foam is the foam index (Dodson 1990, Külaots et al. 2003, Harris et al. 2008, 2008a). The foam index test is currently used by the concrete industry to examine the fly ash for use in concrete. However, there is no correlation to adsorption equilibrium and published correlations to mortar or concrete are limited to low carbon fly ash (Folliard et al. 2009, Lashley 2009).

The standard foam index test used here characterized a range of fly ash by an AEA solution concentration and volume of AEA solution unique to the fly ash type used in each test. The unique initial concentration and volume used produced a 15-second stable foam in the defined time of: within 12 to 18 minutes. The product of the volume of AEA solution used [foam index] and the solution concentration were defined as the *absolute volume* or *absolute foam index*.

Some research suggested that the foam index test is a dynamic test and is not based on equilibrium (Külaots et al. 2003). In addition, some claim that equilibrium characterized with surfactants and fly ash takes hours, whereas the foam index test time is only minutes (Yu et al. 2000). Other research suggested that equilibrium could be reached in as little as 10 minutes, depending on the carbon characteristics in the fly ash (Baltrus and LaCount 2001).

The fly-ash slurry system at a metastable foam is an indicator of the amount of AEA necessary to sustain a foam of a specified duration at a specified time, not the condition of system equilibrium. The foam index was not an equilibrium condition. Equilibrium isotherm equations obtained from direct isotherm tests were used to calculate fly ash capacity using the absolute foam index. The results showed that the calculated fly ash capacity using the absolute foam index was much less than capacities obtained from isotherm tests that were conducted with higher initial concentrations. This indicated that the absolute foam index was not at or near equilibrium. Rather, it was a dynamic test where the time of the test played an important role in the results. The relationship between these foam index tests and adsorption isotherms were examined.

Few published studies have correlated the foam index to mortar or concrete air content. Correlations available in the literature of foam index to mortar or concrete air content use a foam index of fly ash with a loss on ignition (LOI) below 1% (Folliard et al. 2009, Lashly 2009). Few examined AEA dosages (concentrations) that resulted in a maximum air content that could be achieved by a particular cement paste system. This ‘leveling off’ of air content has been attributed to saturation at a particular w/c ratio and formation of bubble bridges between charged particles (Struble 2004) and is compared to adsorption capacity herein (Ahmed 2012). Mortar density decreased when water was replaced by AEA. The maximum mortar air content at the maximum AEA concentration was a function of minimum functional mortar density, as shown by mortar flow measurements. Additionally, the functionality of surfactant in solution, where the critical micelle concentration (CMC) occurs, was examined against the ‘leveling off’ of air content.

4.3 Materials and Methods

4.3.1 Materials

4.3.1.1 Coal Fly Ash and Cement

Coal fly ash used in absolute foam index tests and mortar tests here ranged from 0.17 to 6.06%. The cement used was Lafarge Type I/II cement (Alpena, MI). The cementitious materials were characterized according to ASTM C618-08a *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete* (ASTM 2008) either as a part NCHRP Project 18-13 or materials suppliers. Complete chemical data is shown in Table 4.1.

Table 4.1

Chemical composition of fly ash and cement.

Fly Ash ID	Class	LOI (% wt.)	SiO_2 (% wt.)	Al_2O_3 (% wt.)	Fe_2O_3 (% wt.)	CaO (%wt.)	SO_3 (%wt.)	MgO (%wt.)
FA-8	F	0.17	60.9	25.7	4.66	3.46	0.29	1.12
FA-20	F	0.39	44.8	23.1	9.51	13.6	0.96	2.97
FA-1	F	0.87	61.6	27.9	3.02	0.82	n/a	n/a
FA-10	F	1.26	46.0	23.6	22.3	1.28	0.77	0.99
FA-15	F	1.43	58.9	16.2	4.71	10.2	0.86	3.13
FA-7	F	2.25	53.9	27.7	8.29	1.45	0.29	1.12
FA-40	F	3.35	53.9	26.3	6.24	9.1	1.1	2.28
FA-32	F	6.06	58.7	29.25	5.34	0.99	0.03	0.87
Lafarge Type I/II (PC-1)		1.37	20.1	4.7	2.7	6.9	2.6	2.4

4.3.1.2 Air-entraining Admixtures.

Five AEAs, of four different surfactant types, were used in this study. These AEAs are commonly used throughout the concrete industry. The AEAs are shown in Table 4.2.

Table 4.2

AEAs and chemical information.

Surfactant ID	Surfactant Type
AEA-A	Vinsol Resin
AEA-B	Alpha Olefin Sulfonate
AEA-E	Benzene Sulfonate
AEA-D	Resin/Rosin/Fatty Acid
AEA-C	Resin/Rosin/Fatty Acid

Manufacturer recommended dosages for concrete are listed in Table 4.3. Dosages are listed in ml of AEA per kg of cementitious materials, as suggested by the manufacturer. Dosages are also listed as ml of AEA per ml of total solution for comparison purposes in this study.

Table 4.3

Manufacturer (MFR) recommended AEA dosages for concrete mixtures.

Air-entraining Admixture	ml AEA/kg cementitious	ml AEA/kg cementitious	AEA v/v, ml AEA/ml tot soln	AEA v/v, ml AEA/ml tot soln
	MFR min	MFR max	MFR min	MFR max
AEA-A	16	260	0.00034	0.0056
AEA-C	15	65	0.00032	0.0014
AEA-D	30	200	0.00064	0.0043
AEA-E	30	60	0.00064	0.0013

4.3.2 Methods

Various correlations were performed using foam index test results, adsorption isotherm results, and mortar dosage, air content, and flow results.

4.3.2.1 Foam Index Tests

Foam index tests were performed according to standard test procedures as developed in this study. AEA solutions were made, 2 g of fly ash, and 8 g cement were placed in a plastic bottle with a tight fitting top, and 25 ml of distilled water added. The container was agitated for 30 seconds. Then a cycle was performed as follows: the lid opened, ml of AEA solution added, the container closed, agitated for 10 seconds, the lid opened, and slurry solution examined for a metastable foam.

4.3.2.2 AEA Adsorption Isotherms: Equations

AEA equilibrium correlations were developed from adsorption isotherms according to procedures developed by Ahmed (2012) to determine adsorption capacity of the coal fly ash, namely the carbon fraction. Carbon content of coal fly ash is typically measured by the loss on ignition % (LOI %), which measures the total carbon content by loss of mass at 750°F according to ASTM C311 *Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete* (ASTM 2011). Adsorption isotherms developed by Ahmed (2012) determine capacity because LOI test results may error up to 75% and is not a measure of capacity (Brown and Dykstra 1995, Dodson 1990, Fan 2001; Zhang, 2003).

4.3.2.3 Mortar Mixtures

Mortars were mixed according to ASTM C109/C109M-11a *Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)* (ASTM 2008a). Several batches of mortars were mixed for the same fly ash type increasing only the AEA dosage in each subsequent batch until a point where the next increase in dosage resulted in no increase in air content. The mortar mixtures included Lafarge Type I/II cement (Alpena, MI), various fly ash identified by LOI % in Table 4.1, water, AEAs as shown in Table 4.2 and standard sand meeting ASTM C778-06 *Standard Specification for Standard Sand* (ASTM 2006). Mortars with 25% substitution [by mass of cement] of coal fly ash were prepared. The sand, cement, liquid, and fly ash volumes were identical in every mortar mixture. The fly ash type and the admixture dosage were adjusted.

4.3.2.4 Mortar Air Content

Air contents of mortar mixtures were determined gravimetrically by the ASTM C185-08 *Standard Test Method for Air Content of Hydraulic Cement Mortar* procedure (ASTM 2008b). The theoretical mass per unit volume (g/cm^3) was calculated from mixture materials: sand, water, AEA, cement, and fly ash. Mortar was mixed and immediately placed in to vessels of known mass (g) and the actual mass per unit volume (g/cm^3) was determined. The theoretical mass per unit volume and the actual mass per unit volume were used to calculate the air content of the mortar.

4.3.2.5 Mortar flow

The ASTM C1437-07 *Standard Test Method for Flow of Hydraulic Cement Mortar* was used here for density results verification. Mortar was placed in a mold of specified dimensions on top of a flow table. The mold was removed and the mortar was lifted up to the specified height and dropped 25 times over 15 seconds. The final diameter was measured. Mortar flow was reported as % increase of base diameter from the original base diameter.

4.3.2.6 Absolute Foam Index - Adsorption Isotherm Results Correlation Method

Absolute foam index results were correlated with predicted isotherm equilibrium capacities (Ahmed 2012). This allowed the foam index results and isotherm results to be compared. Chemisorption or irreversible sorption (Sontheimer et al. 1988) in isotherms and foam index test results were also compared.

4.3.2.7 Surface Tension Measurements and Critical Micelle Determination by Surface Tension

The CMC is the surfactant concentration where micelles form and the surfactant molecules agglomerate in the solution. When this condition has been reached, the surfactant molecules are able to minimize their interaction with water (Krüss n.d, Rulison 2001, Tadros 2005).

Critical micelle concentration (CMC) of AEA-A was determined by measuring changes in surface tension using the Krüss G10 goniometer. Surface tension measurements were made on distilled water to calibrate the instrument, and then the surface tension of the solution was determined. A 100% solution consisting of 5 ml of AEA-A was the initial solution. After the surface tension measurements were made, 5 ml of distilled water was added to the 5 ml of 100% AEA-A solution for a 50% or 0.5 ml AEA/ml solution. Next, 5 ml of distilled water was added to the 50% solution for a 0.25 ml AEA/ml solution. Surface tension measurements and dilutions continued in this manner until the CMC was reached. The CMC was the intersection of the concentration dependent and concentration independent surface tensions.

4.4 Results and Correlations

4.4.1 Correlation: Foam Index Results to Adsorption Isotherm Results

Adsorption isotherm equations were used to determine whether or not the absolute foam index was an equilibrium condition. Absolute foam index results are listed in Table 4.4 column 3. For comparison, the absolute foam index was converted to absolute foam index/g. The absolute foam index was divided by 2 because there were 2 g of fly ash in every foam index test. Absolute foam index/g is listed in Table 4.4 column 4.

The theoretical AEA concentration (total vol of stock AEA/total vol of water used) in the absolute foam index test was calculated as if the absolute volume was added all at once. Then this theoretical AEA concentration was divided by 2 for a 'per g of FA' basis for the value in Table 4.4 column 5.

The theoretical AEA concentration from Table 4.4 column 5 was used as the isotherm equilibrium AEA concentration denoted by the x value in the isotherm equation. The y variable in isotherm equations shown in Table 4.5 column 7 was the calculated isotherm equilibrium capacity in terms of ml of AEA/g of fly ash.

Table 4.4

Foam index test results and corresponding isotherm equations for AEA-A.

1	2	3	4	5
Fly Ash ID	LOI %	Absolute foam index (ml)	Absolute foam index/2 (ml/g)	FI Theoretical Concentration/2 (% vol)
FA-8	0.17	0.01	0.005	0.0199
FA-20	0.39	0.0076	0.0038	0.0152
FA-1	0.87	0.0154	0.0077	0.0309
FA-10	1.26	0.011	0.0055	0.0220
FA-15	1.43	0.0292	0.0146	0.0583
FA-7	2.25	0.0123	0.00615	0.0246
FA-40	3.35	0.0285	0.0143	0.0569
FA-39	10.5	0.0468	0.0243	0.0934

Column 3: Absolute foam index, ml

Column 4: Absolute foam index (column 3)/2

Column 5: Theoretical AEA concentration (total vol of stock AEA/total vol of water used) in the foam absolute index test [if the absolute volume was added all at once] for a per g of FA basis.

Example using FA - 8: (100* 0.01 ml /(25 ml + 25 drops * 0.02 ml/drop))/2 = 0.040%/2 = 0.0199%

(100* column 3 /(25 ml + 25 drops * 0.02 ml/drop))/2 = column 5

*Note: Number of drops varied for each fly ash.

Table 4.5

Foam index test results and corresponding isotherm equations for AEA-A.

1	2	6	7
Fly Ash ID	LOI %	Equilibrium isotherm equations (Ahmed, 2012)	Calculated isotherm capacity, y (ml/g)
FA-8	0.17	$y = 0.006\ x^{0.4089}$	0.00121
FA-20	0.39	$y = 0.0068\ x^{0.9081}$	0.000151
FA-1	0.87	$y = 0.0076\ x^{0.516}$	0.00126
FA-10	1.26	$y = 0.0093\ x^{0.398}$	0.00204
FA-15	1.43	$y = 0.0123\ x^{0.2618}$	0.00585
FA-7	2.25	$y = 0.0069\ x^{0.5305}$	0.00097
FA-40	3.35	$y = 0.019\ x^{0.1848}$	0.01119
FA-39	10.5	$y = 0.0658\ x^{0.2027}$	0.04069

Column 6: Equilibrium isotherm equations (Ahmed, 2012)

y: capacity, ml of AEA/g of fly ash

x: initial isotherm solution concentration [AEA solution], % volume

The absolute foam index test and the adsorption isotherm tests quantify the adsorption of fly ash on different basis but a trend does exist as shown in Figure 4.1.

An example comparison of absolute foam index and isotherm results for FA-20 show that the absolute foam index is not an equilibrium condition. Isotherms conducted by Ahmed (2012) on the lowest capacity fly ash FA-20, were performed at initial isotherm solution concentrations as low 0.2% which is higher than the theoretical AEA concentration, 0.0152%. The isotherm capacity at 0.2% was 0.0015 ml of AEA/g as conducted by Ahmed (2012) (FA-20), an order of magnitude higher than the capacity calculated from the theoretical AEA concentration (column 7) 0.000151 ml of AEA/g.

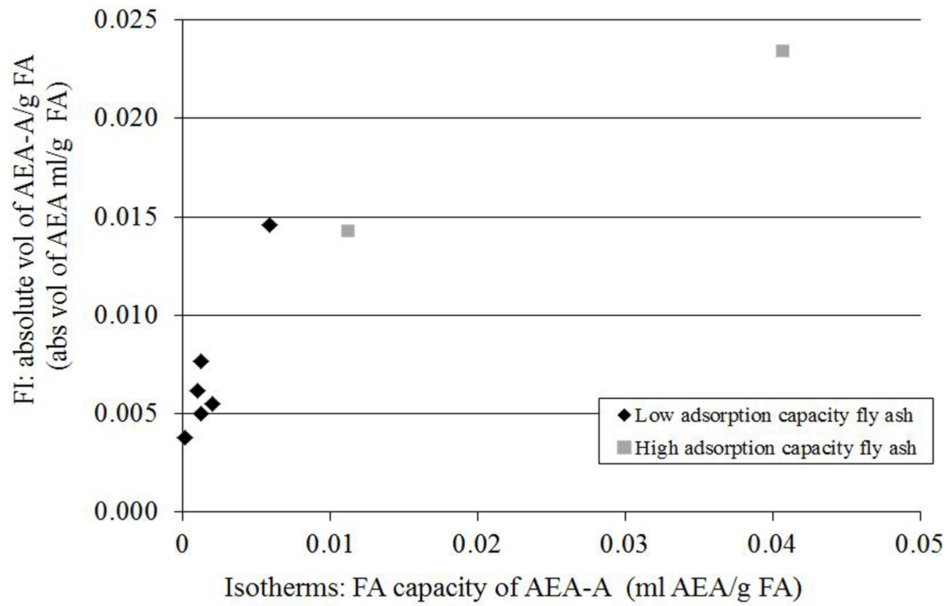

Figure 4.1 Isotherm volume (column 4) versus absolute foam index volume (column 7).

Observations of foam that were made during absolute foam index tests suggested that equilibrium had not been completed; after a 15-second metastable foam had been observed, the container was agitated again without another AEA addition and 15-second metastable foam would not again result. This suggested that the 15-second metastable foam was not at adsorption equilibrium. It is recommended for future work that the other foam indexes be compared to adsorption equilibrium.

4.4.2 Correlation: Absolute Foam Index Results to Maximum Mortar Air

The absolute foam index was compared to the mortar dosage for the system maximum air content on a volume per volume basis. Volumes of materials used in the foam index test and in a mortar mixture were compared in Table 4.6.

Table 4.6

Foam index test materials compared with mortar materials.

AEA-A w/ FA-7	Foam Index Test	Mortar Test
ml of AEA (absolute volume AEA)	0.0123	2.3
Total solution = ml AEA + ml water (solution volume)	25.41	363.82
ml AEA stock/ml solution volume	0.000484	0.006
kg coal fly ash	0.002	0.20212
kg cement	0.008	0.60636
kg cementitious	0.01	0.80848
ml/100 kg	123	276

Several batches of mortars were mixed for the same fly ash type increasing only the AEA dosage in each subsequent batch while reducing the water accordingly. Mortar air test results for each batch showed for each increase in AEA dosage, air contents increased until a point where the next increase in dosage resulted in no increase in air content. This was maximum air content that could be achieved by the particular mortar system; the system reached its air capacity.

The majority of mortar tests were carried out where air contents increased until a point where the next increase in AEA dosage [AEA concentration] resulted in no increase in air content or the saturation limit as shown in Figure 4.2. It should be noted that to achieve the system maximum air content, the dosage of AEA-A exceeded the manufacturer recommended maximum as shown in Table 4.6. [Mortar dosages for system maximum air content for various fly ashes and AEA-C, AEA-D, and AEA-E were determined in the same manner as for AEA-A as shown in Figure 4.2. These are included in Appendix B.]

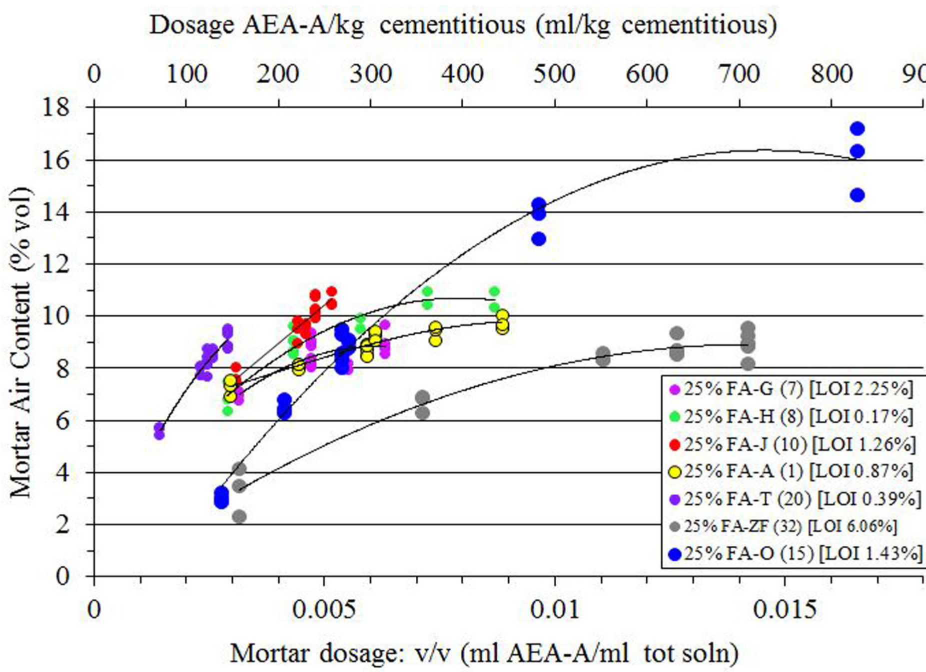

Figure 4.2 Mortar air content versus AEA-A dosage for mortar.

Mortar dosages for system maximum air content were higher for high LOI fly ashes as shown but also higher air contents were achieved. While a larger volume of AEA was necessary to satisfy adsorption capacity of FA-15, additional AEA remained functional in solution due to chemisorption partitioning coefficient for AEA by cement (Ahmed, 2012). Combination isotherms with increased amounts of cement showed higher overall isotherm adsorption capacity.

Mortar dosages for system maximum air content for various fly ashes and AEA-A, AEA-D, and AEA-E were compared to fly ash adsorption capacity as shown in Figure 4.3. The dosage for maximum system air content was greater than the fly ash adsorption capacity for all low carbon fly ash. Changes in surfactant performance occurred at 0.01 ml of AEA per ml of solution for AEA-A where the air content was hindered by AEA dosages above 0.01 ml of AEA per ml of solution for AEA-A; critical micelle concentration range as explained further in Figure 4.5. Once the mortar dosage was higher than 0.01, increased air content was not achieved.

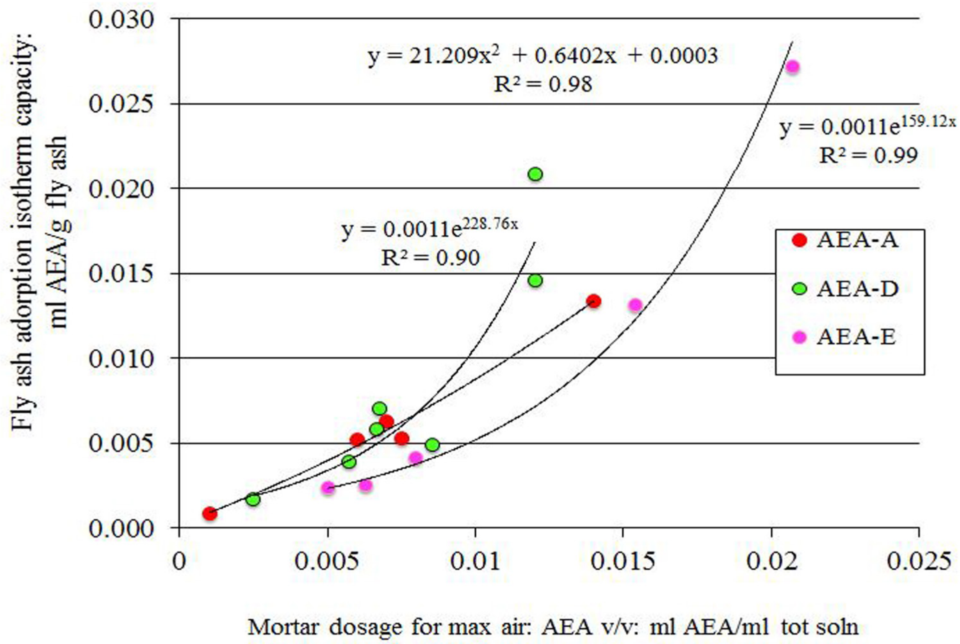

Figure 4.3 Mortar dosage for maximum system air compared to adsorption isotherm capacity.

Changes in performance for AEA-D and AEA-E above 0.01 ml of AEA per ml of solution also occurred. The dosage for maximum system air content was greater than the fly ash adsorption capacity for all low carbon fly ash but above 0.01, increased air content was not achieved.

Critical micelle concentrations for AEA-D and AEA-E should be determined in additional research. A way to measure the volume of functional surfactant in mortar mixtures should be determined.

4.4.3 Verification: Maximum Mortar Air vs. Mortar Flow

Air content was calculated using a unit weight method by first calculating the density. Since air content was related to density in the mortar tests, results of an independent test, the mortar flow test, were plotted for verification. As the concentration of AEA increased, the mortar mixture flow increased synonymous to decreases in viscosity. Results of the mortar flow test are shown in Figure 4.4.

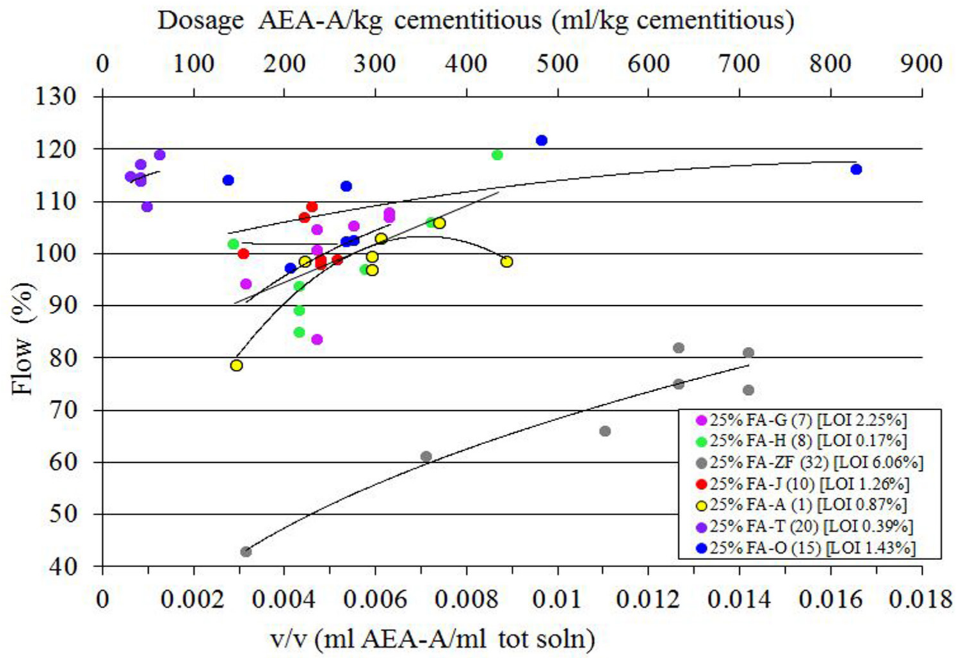

Figure 4.4 Mortar flow versus AEA-A dosage.

Mortar flow increased with AEA dosage for every fly ash-AEA-A mortar mixture except fly ash H. The solution volumes of every mortar mixture performed were equal; the AEA dosage was increased by reducing the volume of water and increasing the volume of AEA. Comparison with results in Figure 4.2 showed that increased AEA dosage to maximum air content or decreased density were similar to trends shown for FA-O, FA-A, and FA-ZF, where mortar flow [or % increased in mortar diameter] increased. The mortar mixture at the maximum flow (minimum density) was where the system could hold the maximum system air content. Mortar flow results for the other mortar mixtures were not as accurate due to the nature of the test. Additional rheological tests should be conducted.

4.4.4 Surface Tension and Critical Micelle Concentration by Surface Tension Results

The manufacturer density of AEA-A was verified by the pendant drop technique using a Krüss G10 goniometer. The density as reported by the manufacturer for AEA-A was 1.03 g/cm^3compared to the measured value of 1.026 g/cm^3.

The Krüss G10 was calibrated with distilled water and the resulting surface tension was 72.5 mN/m. The surface tension reported by the manufacturer for AEA-A was 37.39 mN/m compared to the measured value of 37.28 mN/m for 100% solution. The surface tensions for subsequent surfactant dilutions were also determined by the pendant drop technique.

The critical micelle concentration was determined for AEA-A by plotting the log of the surfactant concentrations as solution volume ratios versus the interfacial surface tension. Three or more surface tension measurements were taken for each AEA-A concentration, and the mean values plotted in Figure 4.5.

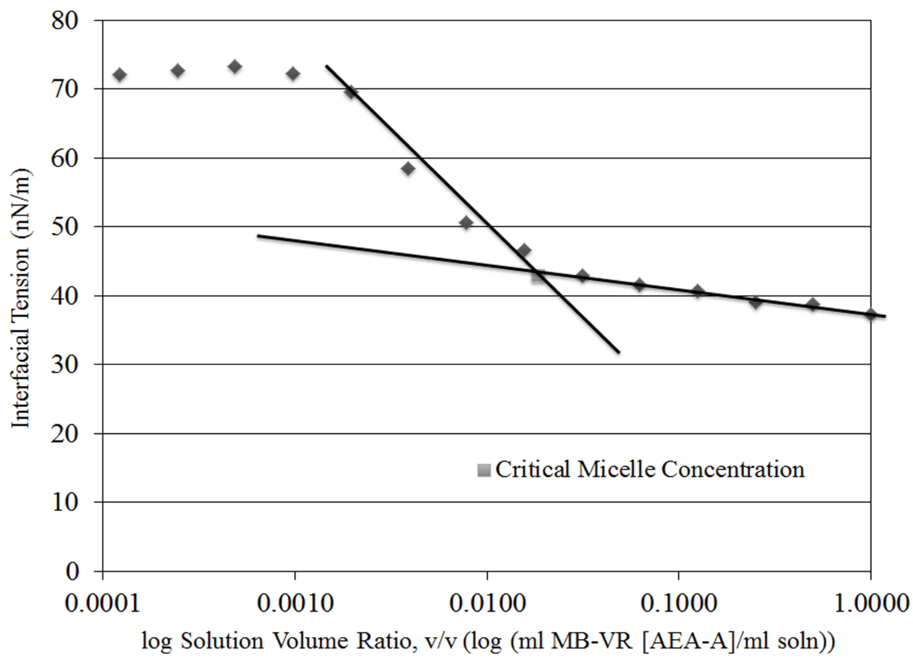

Figure 4.5 CMC of AEA-A: Surface tension measurements.

The intersection of the concentration dependent and concentration independent surface tensions was the CMC. The CMC of AEA-A was estimated to be approximately 0.0185 ml of AEA per ml of solution. Comparing Figure 4.2 and Figure 4.5 showed that the maximum AEA concentration (dosage) for mortar mixtures was where the surfactant changes interfacial surface tension at 0.01 ml of AEA per ml of solution. For the mortar mixtures with fly ash up to 6% as shown here, additional AEA increases in AEA concentration above 0.01 ml of AEA per ml of solution showed no increase in air content.

The concentration calculated for the foam index for FA-7 was 0.000484 ml AEA stock/ml solution as shown in Table 4.6 compared to 0.006 ml AEA stock/ml solution. The difference is an order of magnitude and two orders of magnitude below the CMC.

4.5 Discussion

Calculated results from adsorption isotherm equations indicated that the absolute foam index was not at equilibrium. The foam index was not an equilibrium condition because the isotherm capacities from Ahmed (2012) were greater than capacities calculated from the absolute foam index by an order of magnitude. Even though these tests quantified adsorption of fly ash on different basis, a trend existed between the results. Upon collection of additional data the correlation could continue to be developed to predict fly ash capacity from the foam index.

Additionally, it should be noted that the adsorption isotherm test was designed to account for AEA chemsorption by cement based on cement isotherms performed using different initial concentrations, C_o (Ahmed 2012). The concentrations used in the cement isotherms produced little change in chemisorption when approximately 8 g to 150 g of cement were used for AEA concentrations of 0.2%, 0.4%, and 0.8% by volume (Ahmed 2012). Chemisorption of 0.2% AEA-A in 200 ml of solution could be fully achieved for 8 g of cement in a few seconds (Ahmed 2012). Adsorption however, may take up to an hour for adsorption isotherms (Ahmed 2012) and the absolute foam index was determined in approximately 15 minutes. The theoretical concentrations as converted from the absolute foam index were in the chemisorption concentrations range for all tests as shown in Table 4.4 column 5. This indicated that the absolute foam index may complete chemisorption but equilibrium may not be complete. It is recommended for further research that additional foam index tests be conducted to strengthen the relationship.

The solution volume in every mortar mixture was held constant and mortar flow continued to increase as AEA concentration increased; additional AEA replaced an equal amount of water in solution. Mortar flow results independently showed that increased AEA concentrations were associated with the lower densities. Mortar tests were carried out where air contents increased until a point where the next increase in AEA concentration (dosage) resulted in no increase in air content, or the saturation limit.

Maximum mortar air content was related to the minimum mortar density. The mortar mixture at the maximum flow (minimum density or minimum viscosity) was where the system could hold the maximum system air content. Further rheological studies should be conducted to verify the mortar flow results. A more accurate test method is recommended.

A maximum AEA concentration also corresponded to a minimum density for maximum air content and also a maximum surface tension at stable point or the CMC range. The maximum AEA concentration (dosage) for mortar mixtures was where the surfactant changes interfacial surface tension at 0.01 ml of AEA per ml of solution, or the CMC range. Changes in performance were signified by adsorption isotherm capacity greater than maximum system dosage by AEA dosages above 0.01 ml of AEA per ml of solution for AEA-A. No increases in air content occurred above ml of AEA per ml of solution.

The concentration calculated for the foam index was an order of magnitude below the maximum mortar air concentration and two orders of magnitude below the CMC. Foam index data should be examined against maximum mortar air to find if a correlation exists.

4.6 References

Ahmed, Z. 2012. The Quantification of the Fly Ash Adsorption Capacity for the Purpose of Characterization and Use in Concrete. Doctoral Dissertation. Michigan Technological University, Houghton, MI.

ASTM. 2011. ASTM C311-11a Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete. Annual Book of ASTM Standards. Volume 4.02 Concrete and Aggregates. American Society for Testing and Materials, West Conshohocken, PA.

ASTM. 2006. ASTM C778-06 Standard Specification for Standard Sand. Annual Book of ASTM Standards. Volume 4.01 Cement; Lime; Gypsum. American Society for Testing and Materials, West Conshohocken, PA.

ASTM. 2008. ASTM C618-08a Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. Annual Book of ASTM Standards. Volume 4.02 Concrete and Aggregates. American Society for Testing and Materials, West Conshohocken, PA.

ASTM. 2008a. ASTM C33/C109M-11a Standard Specification for Concrete Aggregates. Annual Book of ASTM Standards. Volume 4.02 Concrete and Aggregates. American Society for Testing and Materials, West Conshohocken, PA.

ASTM. 2008b. ASTM C185-08 Standard Test Method for Air Content of Hydraulic Cement Mortar. Annual Book of ASTM Standards. Volume 4.01 Cement; Lime; Gypsum. American Society for Testing and Materials, West Conshohocken, PA.

Baltrus JP, LaCount RB. 2001. Measurements of Adsorption of Air-Entraining Admixture on Fly Ash in Concrete and Cement. Cement and Concrete Research. 31(5): 819-824.

Binks B. 2002. Particles as Surfactants-Similarities and Differences. Current Opinion in Colloid & Interface Science. Vol. 7, p 21-41.

Brown RC, Dykstra J. 1995. Systematic Errors in the Use of Loss-on-Ignition to Measure Unburned Carbon in Fly Ash. Fuel. 74(4):570-574.

Dodson V. 1990. Concrete Admixtures. Van Nostrand Rienhold: New York, New York. p. 137-162.

Fan M, Brown RC. 2001. Comparison of the Loss-on-Ignition and Thermogravimetric Analysis Techniques in Measuring Unburned Carbon in Coal Fly Ash. Energy & Fuels. 15(6):1414-1417.

Folliard K, Hover K, Harris N, Ley MT, Naranjo A. 2009. Effects of Texas Fly Ash on Air-Entrainment in Concrete: Comprehensive Report. Texas Department of Transportation. Available from http://www.utexas.edu/research/ctr/pdf_reports/0_5207_1.pdf

Harris NH, Hover KC, Folliard KJ, Ley MT. 2006. Variables Affecting the ASTM Standard C 311 Loss on Ignition Test for Fly Ash. Journal of ASTM International. 3(8).

Harris NH, Hover KC, Folliard KJ, Ley MT. 2008. The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part I-Evaluation of the State of Practice. Journal of ASTM International, On-line. 5(7):1-15.

Harris NH, Hover KC, Folliard KJ, Ley MT. 2008a. The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part II-Development of a Standard Test Method: Apparatus and Procedure. Journal of ASTM International, On-line. On-line. 5(7):1-15.

Harris NH, Hover KC, Folliard KJ, Ley MT. 2008b. The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part III-Development of a Standard Test Method: Proportions of Materials. Journal of ASTM International, On-line. 5(7):1-11.

Hunter T, Pugh R, Franks G, Jameson G. 2008. The Role of Particles in Stabilising Foams and Emulsions. Advances in Colloid and Interface Science. 137(2): 57-81.

Krüss. – Critical Micelle Measurement. [Internet]. N.d. Krüss, GmbH, Hamburg, Germany. [cited: July 30, 2010]. Available from http://www.kruss.de/en/theory/measurements/surface-tension/cmc-measurement.html

Külaots I, Hsu A, Hurt RH, Suuberg EM. 2003. Adsorption of Surfactants on Unburned Carbon in Fly Ash and Development of a Standardized Foam Index Test. Cement and Concrete Research. 33(12):2091-2099.

Lashley L. 2009. The Compatibility and Performance of Cementitious Materials and Admixtures. Master's Thesis and PCA report. PCA R&D Serial No. SN3106, Portland Cement Association and University of Toronto, Toronto Canada.

Rulison C. 2001. Technical Application Note 201: Critical Micelle Concentration as a Function of Head Group Size for Alkyl Alcohol Ethoxylates. Newbury, OH: Augustine Scientific.

Sontheimer H, Crittenden J, Summers S, Frick B, Fettig J, Hömer G, Hubele C, Zimmer G. 1988. Activated Carbon for Water Treatment, 2nd Edition. DVGW-Forschungsstelle.

Struble L, Jiang Q. 2004. Effects of Air Entrainment on Rheology. ACI Materials Journal. 101(6):448-456

Tadros T. 2006. Applied Surfactants: Principles and Applications. Weinheim, Germany: Wiley-VCH.

Yu J, Külaots I, Sabanegh N, Gao Y, Hurt RH, Suuberg ES, Mehta A. 2000. Adsorptive and Optical Properties of Fly Ash from Coal and Petroleum Coke Co-Firing. Energy & Fuels. 14(3):591-596.

Zhang T, Lu Z, M.M. Maroto-Valer J.M, Andrésen JM, Schobert HH. 2003. Comparison of High-Unburned-Carbon Fly Ashes from Different Combustor Types and Their Steam Activated Products. Energy & Fuels. 17(2):369-377.

5. Conclusion

A standard procedure was developed that successfully characterized fly ash. This included a foam index test that terminated between 12 and 18 minutes with use of the appropriate concentration per test. The foam index test was an adaption of the Harris foam index test (Harris et al. 2008a) that was formed by studying agitation, and differences in adsorption rates shown by test results where different concentrations were used. The results of the foam index test were correlated with the results of the coal fly ash iodine number (Ahmed 2012) and also mortars as described in this section.

5.1 The Standard Procedure and the Absolute Foam Index Test

The absolute foam index test was modeled after the Harris test because it was the most fundamentally repeatable procedure. Results from this study proved that the adapted procedure offered the lowest coefficient of variation in results with different coal fly ash types. Additionally, the container specified by Harris was easiest to use in the automated Wrist Action Shaker by Burrell (WAS) for standard agitation.

Standard agitation through WAS use consistently resulted in lower overall COV than manual tests performed throughout this study. However, a single operator could perform tests and arrive at results that were acceptable depending on the accuracy desired. If a sequence of tests is performed manually, it is recommended that a single operator perform them.

The ‘certain time’ or test termination time specified in the foam index test designed here was determined experimentally. The test termination time was 15 minutes, or since a metastable foam was subjective, between 12 and 18 minutes. The 15-minute fixed point removed the variable of time and the correct concentration and amount of AEA added to a particular fly ash slurry at a fixed point was found by the foam index indicator. Under those conditions, a constant agitation and a concentration gradient with proportional peaks over a fixed time was found for every test allowing for characterization of different fly ash types.

The true concentration over the duration of the test was not profiled because sampling could not be done during the test due to the low rate of AEA exposure and immediate chemisorption. Equilibrium was not met as proved by calculation completed with equilibrium isotherm equations. Instead, a fixed point in time that was synonymous for every fly ash slurry combination was identified by the foam index. Further research could include devising a rate law. One possibility to form a rate law equation would be a straight-line approach without the variable of time. Another possibility could include devising a way to measure the concentration gradient peaks and troughs through further experimentation.

The absolute foam index test procedure (the goal being a 15-minute endpoint with limits of 12 to 18 minutes) as designed was validated through performance of eighty tests. The eighty tests included tests with five AEAs, three cement types, and coal fly ash samples with a broad range of LOI from 0.25% to 23.3%. Two tests were conducted on each combination and the results were an average of two tests. The average of the two tests was the final measured foam index number for each combination.

Multiple regression analysis was performed on the complete set of eighty test results to find the most frequent satisfying initial concentrations for the final test design while also satisfying the 12 to 18 minute termination requirement. The most frequent satisfying initial concentrations predicted from this analysis were 2%, 6%, 10%, and 15%. This combination contained the least number of concentrations that satisfied all combinations of AEA and fly ash except 5 high carbon fly ash test sets. These concentrations were adopted and specified for use in the proposed standard procedure as designed here for the foam index test. The standard procedure should be used to characterize fly ash as it successfully characterized all fly ash tested here with an appropriate concentration.

5.2 Correlation of the Absolute Foam Index to Other Tests

Part of this study, National Cooperative Highway Research Program (NCHRP) of the Transportation Research Board of The National Academies: Project 18-13: Specifications and Protocols for Acceptance Tests of Fly Ash Used in Highway Concrete, was to correlate the foam index test results with the results of other tests developed in this study. These other tests included ASTM D4607-94 (2006) *Standard Test Method for Determination of Iodine Number of Activated Carbon*, AEA adsorption isotherms, and mortars. Additional correlations and ideas not included in the previous chapter are included here.

5.2.1 Correlation to Iodine Number

ASTM D4607-94 *Standard Test Method for Determination of Iodine Number of Activated Carbon* states that the iodine number is a number that describes the adsorption capacity or the level of activation that carbon possesses (ASTM 2006). This test is usually performed on carbon used for drinking water treatment as the carbon specified for use by this test is reactivated or unused carbon (ASTM 2006). The adsorption capacity of the carbon is measured at a certain target iodine concentration (ASTM 2006). The activated carbon iodine number test uses the point of 80% reduction from the initial iodine concentration or 0.1N iodine solution (ASTM 2006). Ahmed modified the standard iodine number test for this study (Ahmed 2012). Ahmed performed the iodine number test on coal fly ash carbon with a point of 60% reduction (Ahmed 2012) as well as 80% reduction from the initial iodine concentration as specified in ASTM D4607-94. These corresponded to target iodine concentrations of 0.01N (Ahmed 2012) and 0.005N respectively (ASTM 2006).

The absolute foam index for 10 of the fly ash samples shown in Table 2.**7** [represented as absolute volume of AEA-A], were plotted against iodine numbers [represented by mg iodine per gram of fly ash] for the same 10 fly ash samples. The absolute foam index correlated with iodine isotherm results for both target concentrations as shown in Figure 5.1.

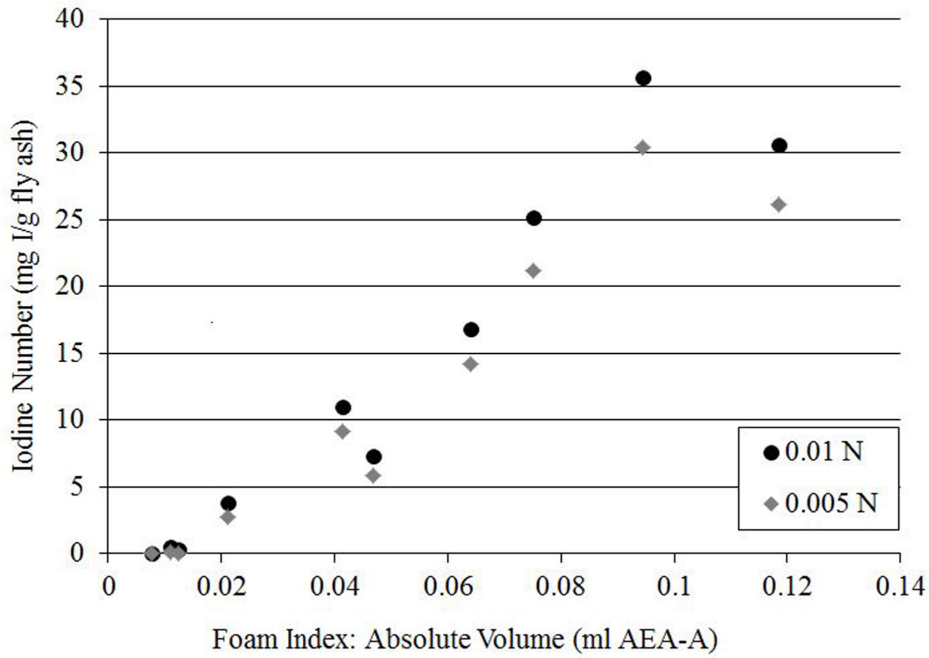

Figure 5.1 Iodine numbers (mg iodine per gram of fly ash) versus absolute foam index.

The iodine number (mg iodine per gram of fly ash) also correlated with LOI % (Ahmed 2012) just as well as the absolute foam index of AEA-A as discussed previously in Section 3.6.

Even though a correlation exists in Figure 5.1 the absolute foam index drops off at 0.12 because the foam index test is subjective and not a true measure of capacity. It has been shown that as compared to the direct isotherm test, the absolute foam index is not fly ash capacity. Adsorption still takes place at the end of the foam index test and could continue if additional AEA were available in solution.

5.2.2 Correlation to Direct Adsorption AEA Isotherms

Iodine isotherms provided an indirect estimate of capacity of fly ash carbon while AEA isotherms provided a direct measure. Coal fly ash was exposed directly to specific AEA concentrations (AEA and water solutions) and the capacity of the carbon measured by the amount of residual AEA left in solution after exposure to fly ash. The capacity was used to provide concentration (dosage) adjustments for required air void contents in mortar and concrete mixtures (Ahmed 2012). This was the reason the foam index parameters were examined more closely against the direct adsorption isotherm parameters as discussed previously in Section 4.4.1.

The isotherm capacities as shown by Ahmed (2012) (FA-20), are an order of magnitude higher than capacities calculated from the theoretical AEA concentration as calculated from absolute foam index tests. Therefore the absolute foam index is not an equilibrium condition.

5.2.3 Correlation to Mortar Mixtures

Mortar mixtures at AEA saturation and maximum air content on volume of AEA per volume of solution basis were shown previously in Figure 4.2. The mortars shown in Figure 4.2 use the same volume of solution (water plus AEA). The resulting differences in air content were achieved by changing the AEA concentration. Additional mortars proved AEA performance was not only dependent on the volume of AEA but also the volume of solution present (water plus AEA).

AEA performance was shown by comparing mortar mixtures using the parameter that is well-known in the concrete industry, w/c or water to cement ratio and also volume of AEA per volume of solution are shown in Figure 5.2 and Figure 5.3. Initial aggregate moisture content and aggregate gradation [and temperatures of all materials] were held constant for all mortar mixture results shown in Figure 5.2 and Figure 5.3 while w/c ratios and AEA dosages varied.

The available solution or w/c ratio and AEA concentration (dosage) directly impacted the air content as shown in Figure 5.2. When the w/c was low, 0.38, not enough solution was available for either concentration of AEA to maximize its potential and the same air content resulted. As w/c increased, less AEA was necessary to produce the same air content as shown by the mixture containing 3.5 g of AEA at w/c 0.43.

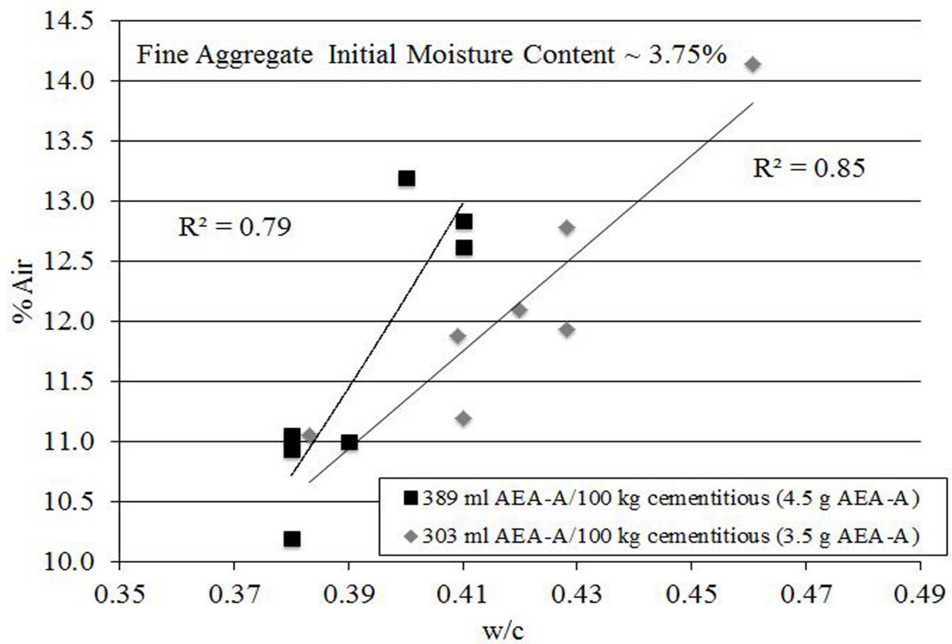

Figure 5.2 Air content results (%) for mortar mixtures with varying AEA dosage and water to cement ratio.

The same comparison on a volume of AEA per volume of solution basis confirmed that higher air contents resulted at lower concentrations of AEA and higher solution volumes.

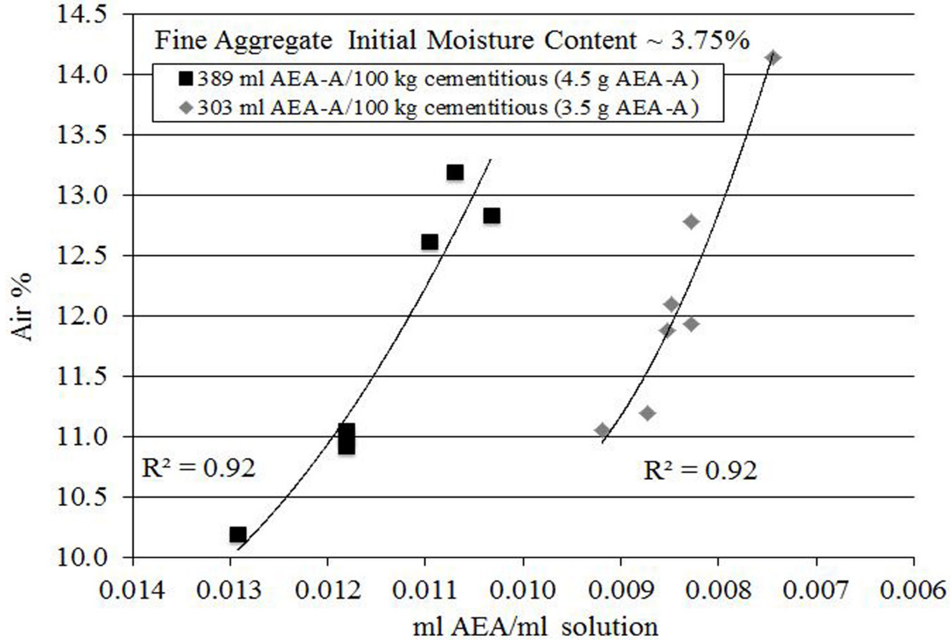

Figure 5.3 Air content results (%) for mortar mixtures with decreasing AEA to solution volume ratio (ml of stock AEA/ml of total solution).

From Figure 4.2 and the results in Appendix B, mortar dosages for system maximum air content were plotted again the absolute foam index in ml of AEA/ml of solution and the following relationships resulted as shown in Figure 5.4.

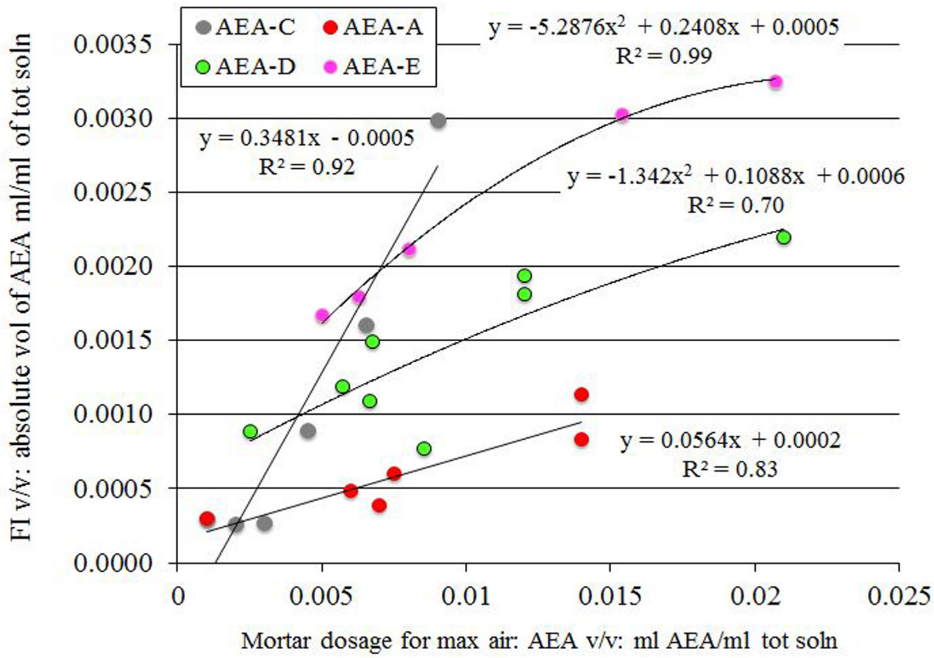

Figure 5.4 Mortar dosage for system maximum air content correlation with absolute foam index in ml of AEA/ml of solution for various fly ashes.

The difference in solution volume between mortar at maximum air and foam index occurrence was approximately a factor of 10, or 0.005 volume of AEA per volume of solution versus 0.0005 volume of AEA per volume of solution, as shown in Figure 4.4. The absolute foam index took 2.5 times less volume of AEA per 100 kg of cementitious materials because performance was higher in the system with more water. This confirmed the difference in ability for the AEA to perform in each system.

The relationship between maximum AEA dosage and the absolute foam index in Figure 5.4 showed that once the absolute foam index was determined, the maximum air content could be determined for mortar systems regardless of fly ash LOI %. However, the mortar mixtures shown in Figure 5.4 were only performed for one w/c ratio and Figure 5.2 shows that AEA performance is a function of available solution or w/c ratio. This relationship should be further examined by performing mortar mixtures for maximum air at other w/c ratios to find the best correlation to the absolute foam index. Additionally, mortars should be made with cement only and the relationship with the foam index determined.

It should be noted that only the material system differences effects on performance were studied here, but the effects of mixing mechanics on performance should not be ignored. To what degree the mixing mechanics affect performance is left for further research.

5.3 Further Research

Physical chemistry explained that change in interfacial or surface tension was a common indicator of CMC (Atkins and de Paula 2006). The surfactant concentration required to produce maximum foam in a slurry system could be a function of the critical concentration (CMC) that can be measured by change in interfacial surface tension (IFT) (Jakubowski 2008). Investigations of critical micelle concentrations of surfactant solutions should be further investigated to explain the relationship of mortar air, the foam index indicator, and also if a relationship exists with equilibrium isotherms.

Concentration of solution or w/c ratio and AEA dosage affected AEA concentration required for an absolute foam index and mortar air as concluded with this research. Further research is necessary to understand differences in the slurry solutions of the foam index test and mortars including but not limited to: mixing types and affects, impacts of cementitious materials and fine aggregates on slurry systems.

Free lime and sulfur exist in fly ash and caused interference when the iodine number test, ASTM D4607-94, was used to measure the adsorption capacity of coal fly ash carbon. The sulfur interfered with the results acquisition and lime possessed the ability to basify the test solution. Basification changed iodine to iodide and inaccurate readings occurred. As a result, a method to alter the coal fly ash to remove the sulfur and free lime without changing the coal fly ash carbon adsorption properties was devised and thus a modified iodine number test specifically for fly ash carbon resulted (Ahmed 2012, ASTM 2006).

Related research of solid-liquid adhesion at a solid-liquid interface linked surface tension to free energy and showed the ability to describe a particular liquid's free energy and polar components, or dispersive, acid, and base components upon interaction (Rulison 1996, van Oss 1988). Further research in this area should be conducted on the interaction of fly ash and solution to explain the basification.

While the basification in the presence of an iodine solution warrants further research and explanation, the fly ash-surfactant interface in regards to optimum w/c ratio and concentration relationships for foam index tests or desired air in mortar also warrants further research using solid-liquid interfacial theories.

Research conducted on surfactant-substrate interfaces indicated that since surfactants are made up of various components, they had the ability to not only change surface tension but also caused change in interfacial energies. These changes caused subsequent changes in the advancement of the surfactant at the contact point (three phase) or the meniscus of the contact angle at the solid liquid interface, i.e. irregular adsorption (Labajos-Broncano et al. 2006). Further research should be conducted to quantify the effects at the solid [coal fly ash]-surfactant interface and their relationship to mortar air and absolute foam index.

Test results published on use of bone char for removal of fluoride and arsenic as an inexpensive media in developing countries shows promise (Brunson et al. 2009, Mlilo et al. 2010). Similar to fly ash, many varieties and compositions exist and extensive studies have characterized several samples using well known techniques such as specific surface area determination, x-ray diffraction analysis, scanning electron microscopy, digestion, and as previously mentioned batch experiments (Mlilo et al. 2010). Batch studies have proven that bone char successfully removes undesirable materials (Brunson et al. 2009, Mlilo et al. 2010). Also similar to tests with coal fly ash (Ahmed 2012), measurement of residual concentrations to assess the adsorption capacity of bone char can be quite complicated (Mlilo et al. 2010). The foam index test is a simple test that successfully characterized coal fly ash with appropriate surfactant concentrations. Since it is a simple test, with further solid-liquid interfacial research, the foam index test could be modified for use with bone char to be a simple field test that could be used to indicate successful source for water treatment.

5.4 References

Ahmed Z. 2012. The Quantification of the Fly Ash Adsorption Capacity for the Purpose of Characterization and Use in Concrete. Doctoral Dissertation. Michigan Technological University, Houghton, MI.

Atkins P, de Paula J. 2006. Physical Chemistry, 8th Edition. New York, NY: W.H. Freeman and Company.

ASTM. 2006. ASTM D4607-94 Standard Test Method for Determination of Iodine Number of Activated Carbon. Volume 15.01 Refractories, Activated Carbon; Advanced Ceramics. American Society for Testing and Materials, West Conshohocken, PA.

Brunson LR, Sabatini DA. 2009. Evaluation of Fish Bone Char as an Appropriate Arsenic and Fluoride Removal Technology for Emerging Regions. Environmental Engineering Science. 26(12):1777-1784.

Harris NJ, Hover KC, Folliard KJ, Ley MT. 2008a. The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part II-Development of a Standard Test Method: Apparatus and Procedure. Journal of ASTM International, On-line. On-line. 5(7):1-15.

Jakubowski H. - Chemistry and Society: Intermolecular Forces (IMF) and Solutions. [Internet]. 2008. College of St. Benedict/St. John's University, Collegeville, MN. [cited: July 30, 2010]. Available from http://employees.csbsju.edu/hjakubowski/classes/Chem%20and%20Society/IMF_Solutions/olIMF_solutions.htm

Labajos-Broncano L, Antequera-Barroso JA, Gonzalez-Martin ML Bruque. 2006. An Experimental Study about the Imbibition of Aqueous Solutions of Low Concentration of a Non-Adsorbable Surfactant in a Hydrophilic Porous Medium. Journal of Colloid and Interface Science. 301(1):323-328.

Mlilo TB, Brunson LR, Sabatin DA. 2010. Arsenic and Fluoride Removal Using Simple Materials. ASCE Journal of Environmental Engineering. 136(4):391-398.

Rulison C. 1996. Technical Application Note 402: Wettability Studies for Porous Solids Including Powders and Fibrous Materials. Newbury, OH: Augustine Scientific.

Appendix A: Chapter 3 Supplemental Information

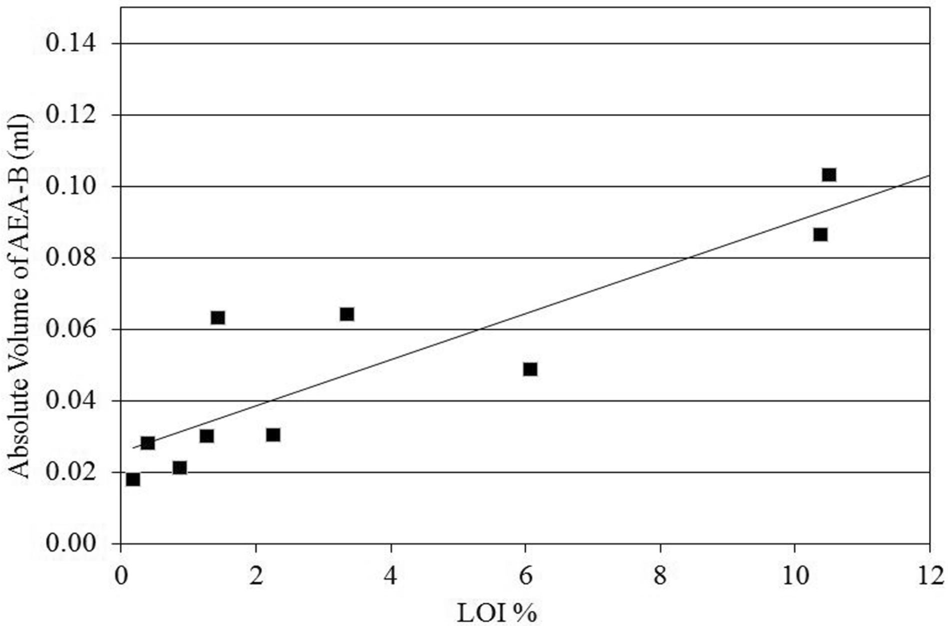

Figure A.1 The AEA-B absolute foam index (ml) versus ten fly ash samples with LOI ranging from 0.39% to 23.30% where R^2 = 0.77.

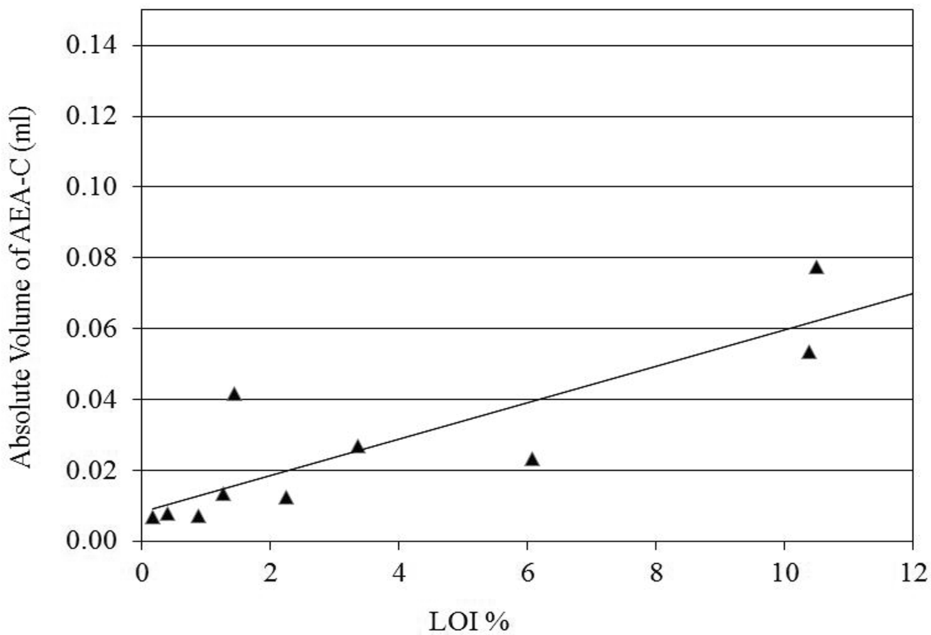

Figure A.2 The AEA-C absolute foam index (ml) versus ten fly ash samples with LOI ranging from 0.39% to 23.30% where R^2 = 0.74.

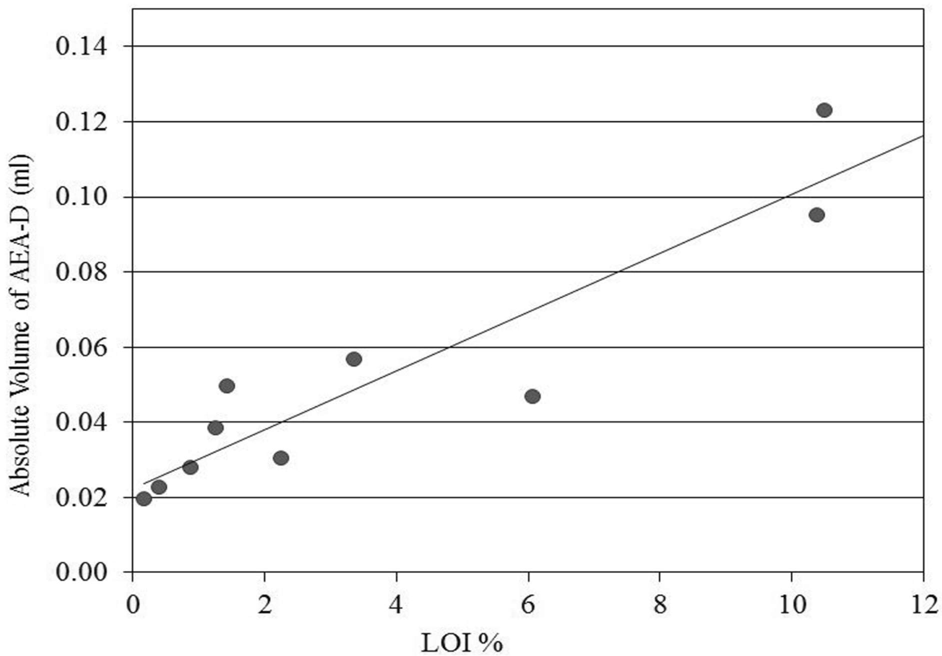

Figure A.3 The AEA-D absolute foam index (ml) versus ten fly ash samples with LOI ranging from 0.39% to 23.30% where R^2 = 0.86.

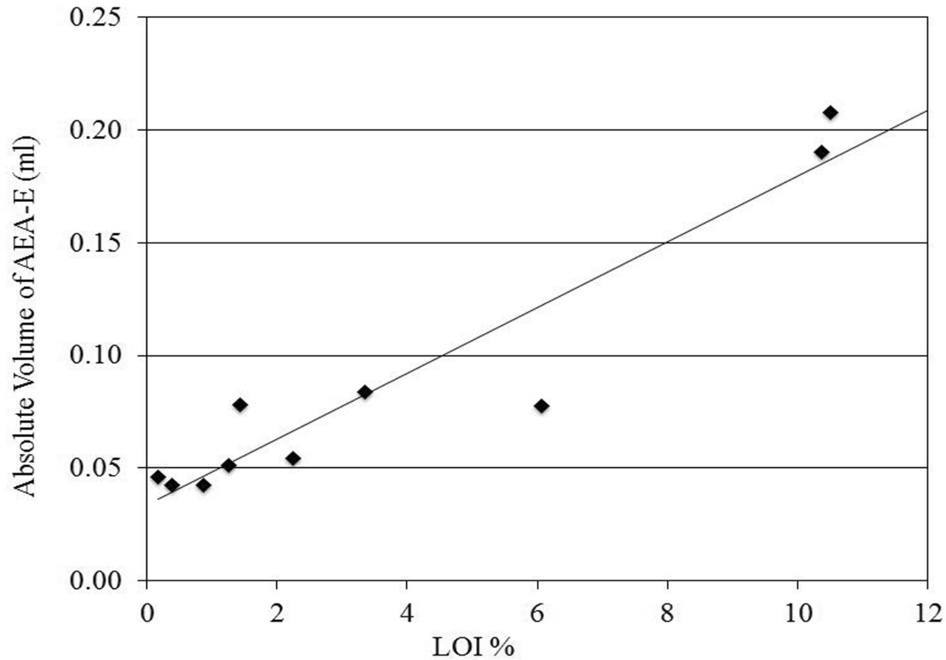

Figure A.4 The AEA-E absolute foam index (ml) versus ten fly ash samples with LOI ranging from 0.39% to 23.30% where R^2 = 0.90.

Appendix B: Chapter 4 Supplemental Information

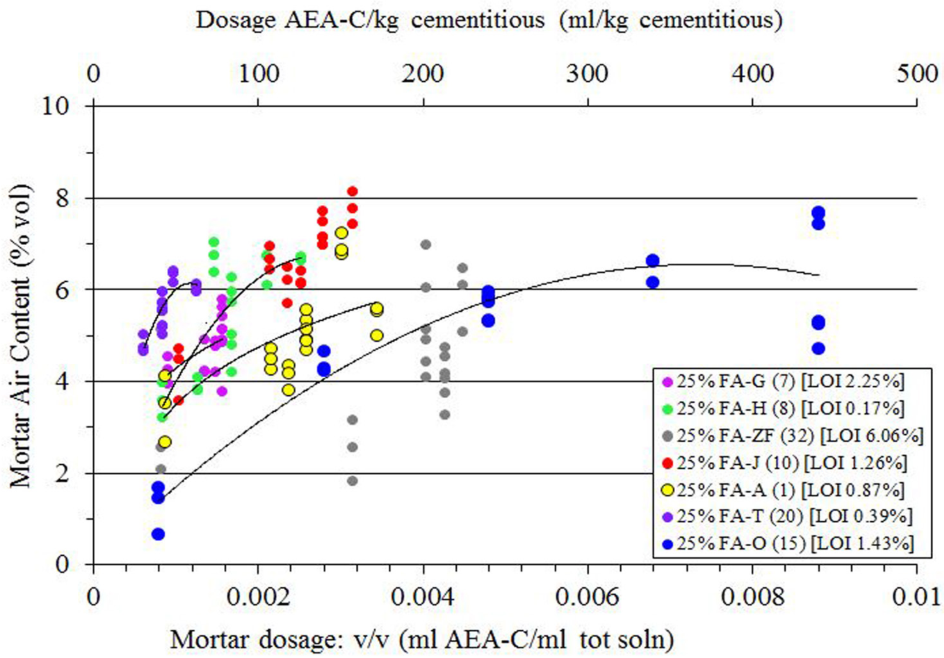

Figure B.1 Mortar air content versus AEA-C dosage for mortar.

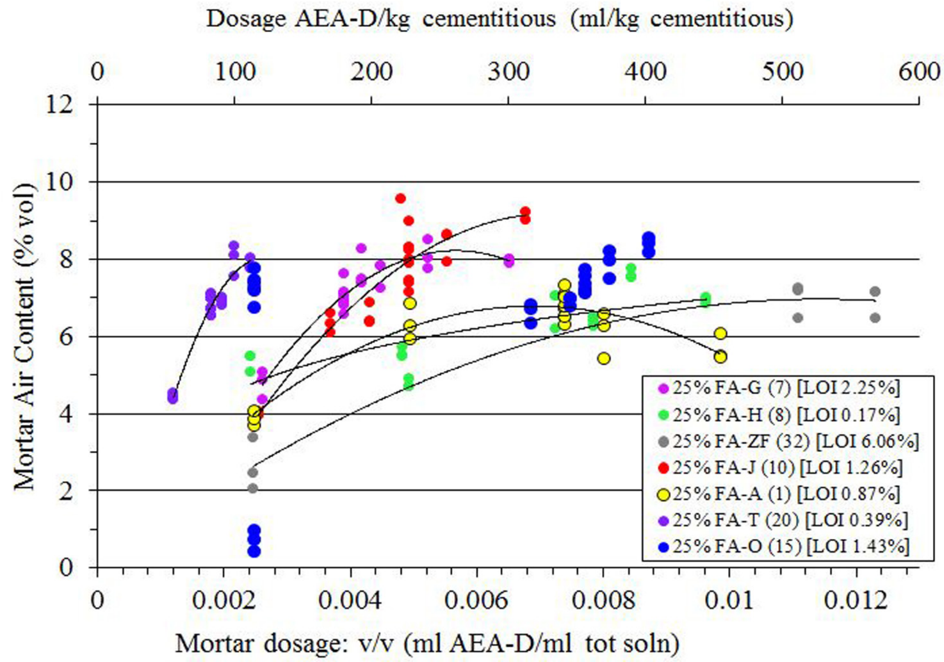

Figure B.2 Mortar air content versus AEA-D dosage for mortar.

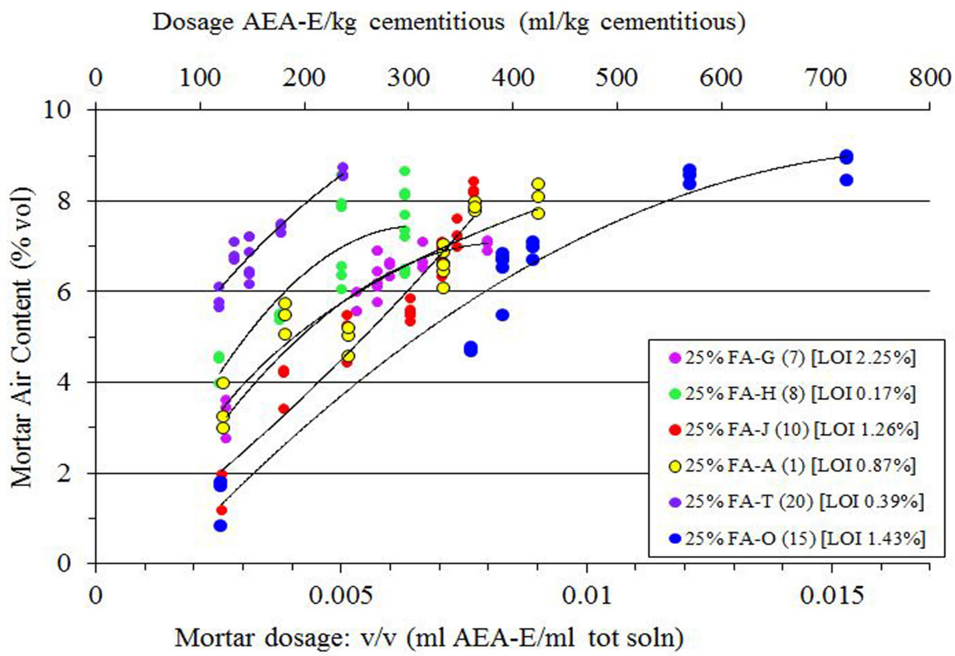

Figure B.3 Mortar air content versus AEA-E dosage for mortar.

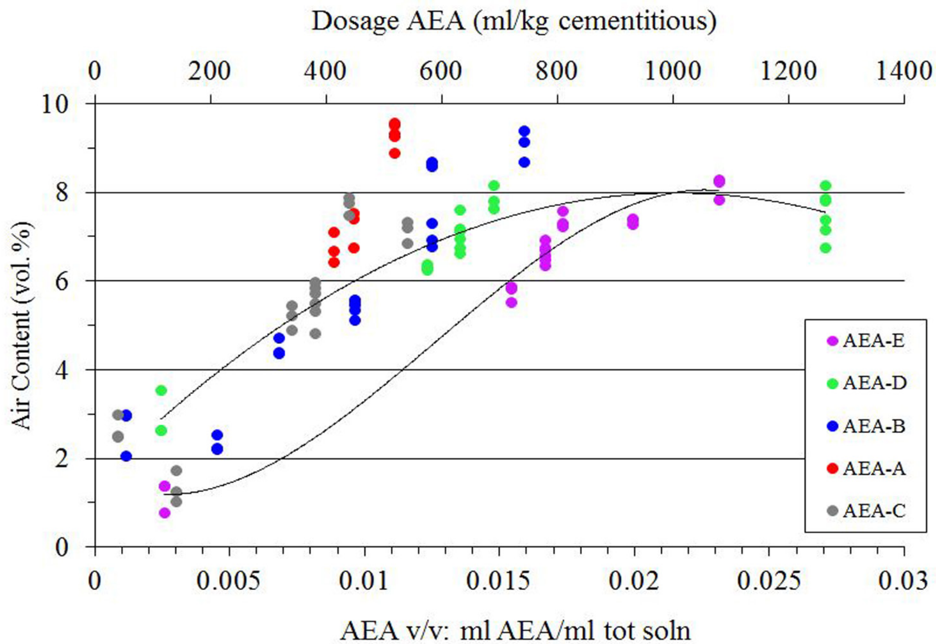

Figure B.4 Mortar air content of FA-ZN(40) versus dosage for mortar.