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Automated foam index test: Quantifying air entraining agent addition and interactions with fly ash–cement admixtures

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ABSTRACT

The use of a new automated foam index test (AFIT) instrument is discussed as a quantitative approach to observe air entraining agent (AEA) interactions with and to measure proper AEA dosage into cement–fly ash mixtures. Based on measuring acoustic emission from bubbles bursting on top of and in water–cement–ash mixtures after AEA addition, AFIT uses computer control to automate steps taken and quantities used during foam index testing, including: water addition; AEA titration; admixture agitation; and acoustic emission data acquisition. Variation of these steps is investigated relative to determining the dynamics of AEA adsorption onto the solid surfaces within water–cement–ash mixtures. Working within time durations needed for AEA equilibration, different water dilution and titration levels of AEA helped elucidate influences of equilibration on the AFIT-determined foam index values. A mathematical discussion about AFIT foam index curves is offered that relates changes in foam stability to surface tension and interactions with free calcia as AEA's are titrated into ash and cement–ash mixtures. Correlations between experimental surface tension data and the foam index curves are also presented. The potential of applying the AFIT to control air content in concrete with and without fly ash is also examined relative to using the C231 ASTM testing procedure on concrete mixes.

1. Introduction

The dual hydrophilic/hydrophobic nature of surfactants is beneficially exploited in many industrial processes and formulations, and in cleaning and foaming applications. In the US concrete industry, surfactants called air entraining agents (AEA's) are commonly used in concrete mixes to instill small, stable air bubbles that increase workability and resistance of the hardened material to freeze/thaw cycles [1–4]. Control of the dosing of AEA into concrete mixtures starts at ready mix plants and ends at construction sites where contract specifications are to be met. Many factors affect its efficacy, including material properties such as cement alkali levels, cement fineness, sand and aggregate size distribution and sand-aggregate ratio; the presence of chemical admixtures such as water reducers, retarders, accelerators and plasticizers/superplasticizers; the presence of mineral admixtures such as combustion fly ash and silica fume; and, the methods used during concrete conveyance, consolidation and finishing [5–9]. It is therefore not surprising that manufacturers and suppliers of AEA's do not specify exact quantities of AEA to be used in concrete mixes for meeting specified air contents. Using appropriate amounts of AEA is imperative: too much creates excessive air void volume which can decrease concrete strengths to levels below contract specifications.

To date, AEA usage at ready mix plants has typically relied on experience-based operations related to mixing concrete to have ~5–8% air content when using cement, sand, aggregate and other constituents that can have relatively constant physical and chemical characteristics. However, the increased use of pozzolanic mineral admixtures like fume silica and, particularly, coal combustion fly ashes add to the complexity of properly dosing AEA.

In the US during 2005 over 15 million tons of fly ash was consumed primarily in concrete and concrete products [10] where its use is well known to beneficially impact the physical, chemical, economic and environmental aspects of concrete [11–13]. Nevertheless, the constituents within fly ash, particularly the unburned carbon — as usually measured by loss on ignition (LOI) measurements — has been described to absorb AEA more aggressively than do the cement, sand or aggregate constituents [14–18]; thereby, the creation of the required air content when using fly ash may be seriously affected unless AEA dosages are changed compared to when not using fly ash. Furthermore, although ASTM C-618 [19] specifies limits typically applied in the US on the LOI of fly ash to be used as a mineral admixture, AEA demand in concrete mixes may be substantially different when two different fly ashes are admixed into the concrete even though they had identical LOI's. Reasons for these differences have been examined quite extensively [15–18] and relate to the widely

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Table 1
Constituent concentrations in combustion ashes tested.

Silicon oxide	45–55
Aluminum oxide	25–30
Iron oxide	2.0–5.8
Calcium oxide	0.8–1.2
Magnesium oxide	0.2–3.1
Titanium oxide	0.1–0.5
Vanadium oxide	0.1–0.2
LOI	1.2–17.8

variable physical and chemical properties of unburned carbon and minerals that control the propensity to absorb AEA. It would be beneficial if a repeatable, automatic analytical method was available to measure and/or control required AEA dosages.

Some work has been done to develop spectroscopic methods that quantify AEA uptake by fly ash and cement–ash mixtures [21,16,20]. In an ultraviolet–visible (UV–Vis) spectroscopic procedure the latent liquid on an ash or cement–ash mixture is removed after mixing it with a prescribed amount of AEA, and then the liquid is spectroscopically analyzed relative to known AEA-liquid concentrations. No widespread commercial use of a UV–Vis method for AEA uptake quantification is known.

Another method that has been used for estimating the propensity of mixes to absorb AEA is the foam index test [21]. As commonly practiced, dilute ash–water mixtures with or without cement are incrementally dosed with AEA, in between which the foam created on the surface of the mixture is observed for stability and/or uniformity. Studied comprehensively with a goal of establishing a standardized approach for foam index applications in the concrete industry [17], significant insight was generated that focused on the influence of carbon physical and chemical properties relating to AEA adsorption. However, the reliance on visual observations that are strongly influenced by subjective opinions may impact the potential 'standardized' aspects of the test.

The foam index test involves thorough mixing of dilute mixtures after titration of AEA, thereby maximizing the extent of intimate contact between the surfactant and AEA absorption sites. Theoretically, it should be possible to quantify the capacity of constituents within cement, ash and mixtures thereof to absorb AEA, if subjectivity could be eliminated, because when absorptive sites are saturated with surfactant or other surfactant-uptake reactions are complete [20] any additional adsorption of AEA on these sites should be hindered. Then, AEA available in excess of site saturation is available for lowering the surface tension of the water within the mixture and, upon aggressive agitation, stable bubbles will begin to form on top of the mixture. A recent report confirmed changes in surface tension of the liquid layer when sodium dodecylbenzene sulfonate surfactant was titrated into cement–ash–water mixtures [22].

During foam index tests and at low AEA dosages, unstable bubbles can be observed that actively burst on the liquid surface within ~5–20 s after titration/agitation. Aggressive bubble instability would be expected if the surface tension of the liquid increased as surfactant was consumed by adsorption sites in the solids. This instability suggests that AEA adsorption onto the solid surfaces is a dynamic process, as has been discussed [20,22], that requires an equilibration time greater than that for decreasing surface tension within the liquid layer. Upon saturation of the AEA absorptive sites, bubble stability on the liquid surface should be dramatically improved because the surfactant is able to maintain a decreased surface tension in the liquid. Although bubble bursting is still observed at these higher AEA dosages, and may be partially a result of liquid drainage and wall thinning, their stability improves to the extent that multiple layers of bubbles begin to be observed on top of cement–ash–water mixtures.

Whether the visual foam index test actually determines the ultimate uptake of AEA on fly ash or cement–ash mixtures has been seriously questioned [20,22]. This research, using UV–Vis spectroscopic and surface tension procedures, suggested the time of AEA equilibration with solid adsorption sites was between 15 s to greater than 30 min. Other research pointed to the possibility that it may be as long as one hour [16]. Such differences may be related to physical and chemical differences of the samples studied because diffusion within particles control AEA equilibration [14–18,23] as does the formation of semi-stable salts during the interaction of AEA with free Ca^{2+} and Mg^{2+} ions [20]. However, the UV–Vis and surface tension techniques or the manual foam index tests methods used to date have not dynamically measured AEA equilibration times.

It is well known that commonly-practiced visual foam index test methods are subjective and prone to imprecision. A key to eliminate this subjectivity is the development of an automated and non-intrusive, analytical method that eliminates visual observation of bubble instability. Furthermore, visual foam index testing typically involves manual titration and stopwatch techniques which also impart subjectivity. Fortunately, bursting bubbles emit sound or acoustic emission (AE). By combining commercially-available AE hardware with computer controlled agitation, AEA titration and AE data collection, subjectivity could be eliminated and, possibly, quantitative analytical information acquired.

Hence, this manuscript describes the development of an automated foam index test (AFIT) instrument that is based on detecting sound waves from bursting bubbles. It presents a comparison of AFIT-derived foam index data with surface tension data; describes the need to test cement–ash mixtures rather than just ash by itself if cement–ash interactions are to be elucidated and the amounts of AEA to be used in concrete are to be measured; discusses the dynamic and analytical capacity of AFIT that provides a measure of AEA saturation of adsorption sites within dilute water–ash and water–cement–ash mixtures; discusses differences in equilibration times and dependencies of foam index values on AEA dilutions used during titration; and, derives a mathematical approach that relates the measurement of acoustic emission with foam index and surface tension data.

2. Experimental

2.1. Ash characteristics

Results from ten different, commercially-obtained ASTM-classified Class F fly ashes are presented within this manuscript; their elemental characteristics and loss-on-ignition (LOI) values are given in Tables 1 and 2. They were tested by themselves and in cement (Type I/II Portland cement)–ash mixtures using AFIT procedures described below. The AEA's used were sodium dodecylbenzenesulfonic acid (SDBS), vinsol resin (VR) from Master Builders Company, Cleveland, OH and MicroAir® (MA) also from Master Builders with dilutions between 1:1 water:AEA to 100:1 water:AEA. They were tested because they are commercially available and represent well-known surfactants used in research and within commercial ready-mix operations.

Table 2
Ash labels, LOI's and AEA's used during AFIT, surface tension and air content data acquisition.

	LOI, %	AEA used
Ash1	4.4	VR & SDBS
Ash2	1.7	VR & SDBS
Ash3	2.3	VR & SDBS
Ash4	5.2	VR & SDBS
Ash5	2.9	VR
Ash6	4.7	VR
Ash7	3.9	VR
Ash8	5.1	VR & MA
Ash9	6.9	MA
Ash10	5.9	SDBS

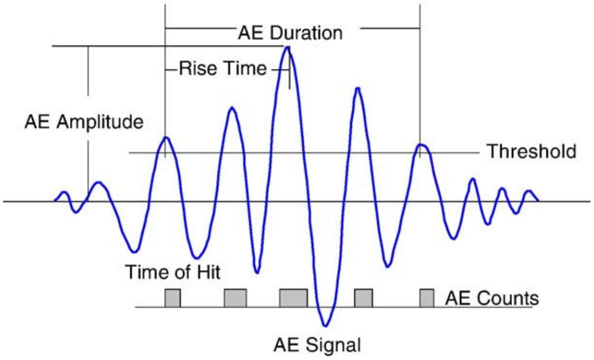

Fig. 1. Characteristics of an acoustic wave.

2.2. Foam index testing and materials

The bursting of a soap or surfactant bubble is accompanied by the release of an energy pulse having acoustic frequencies in the range of ~500–15,000 Hz. A pictorial representation of such a pulse or acoustic wave is presented in Fig. 1. It has characteristics, included amplitude, duration, and rise time and frequency that can be measured using standard microphones, hydrophones or contact sensors in conjunction with specialized computer hardware and software. The non-intrusive capacity of contact sensors, typically based on piezoelectric transducers, was particularly attractive because they can be mounted on the outside of containers to 'listen' to what is occurring within them. This non-intrusive configuration was used on the constructed AFIT instrument shown in Fig. 2.

The AFIT cell, in which ash, cement, water and AEA are mixed, is contained within a sound-proof enclosure when a cover is closed. In it is a stir propeller that is connected to a motor mounted onto the cell lid. The cell volume was 500 ml for the testing described herein. Attached to the side of the cell is a piezoelectric contact sensor, purchased from Physical Acoustics Corporation (Princeton Junction, NJ). Output of the sensor is connected through a sound board; software enables the counting of the number of acoustic waves (called an Event in the following data) detected by the sensor and from bubbles bursting within mixtures contained in the cell. These acoustic waves were counted only if they were above a minimal threshold level (see Fig. 1) determined during baseline AE data acquisition before cement–ash–water mixtures were placed in the cell. Each acoustic wave associated with an Event is also stored, thereby enabling the calculation of emission frequencies during post-test assessment using Fourier transform analyses. A plot of Events-versus-ml of added AEA is displayed during each test, a typical result of which is presented in Fig. 3. Upon concluding a test, the foam index value can be displayed in user-requested units such as ml AEA-per-kg or drops AEA, etc.

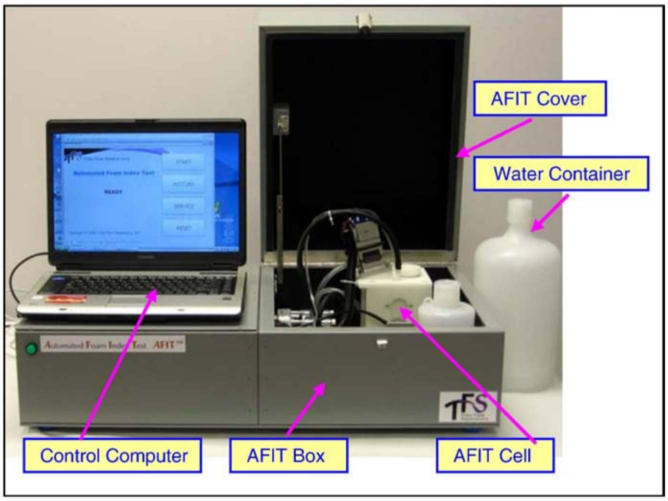

Fig. 2. Overall view of the AFIT instrument with laptop computer.

For the tests described herein the ash or cement–ash mixes were between 20–80 g and the added water was 200 ml. Hence, the solids/water mass ratios were between 0.1-to-0.4, values of which are typical of those used during manual foam index testing. After a solid sample is added to the cell, the AFIT software and hardware are activated and take over adding water to the cell, agitating the mixture, establishing the number of AE Events before AEA is added, and then in a stepwise manner titrating AEA-agitating-acquiring AE data until the foam index value is established. After test completion, a drain and rise cycle is activated that washes the cell making it ready for the next sample. Computer control allows AEA titration levels to be accurately set or changed and the period of AE data collection after each titration to be precisely set or changed.

During initial development of the AFIT instrument the foaming properties of ash and cement–ash mixtures were observed to determine if a relationship existed between visual bubble stability and the number of acoustic events as measured by the acoustic signal of the instrument. These combined AFIT-visual foam index tests established that the peak in the number of Events from the AFIT instrument correlated with visual observation of a metastable and uniform foam on top of the solid/water mixtures. However, it must be realized that acoustic waves generated by bursting or collapsing bubbles and measured with the AFIT instrument include those from both on top and underneath of foam surface layers, not just on top of the foam as is observed during the visual procedure.

In the tests performed, it was typical to use AEA-water titration doses between 0.05 and 5 ml. Computer controlled time sequencing during the testing was also varied; for example, the time durations associated with sequencing included AEA titration (between 0.5 to 6.0 s, dependent on the amount of AEA titrated); agitation (constant at 20 s); soaking (constant at 7 s); and then AE data acquisition (constant at 45 s). Hence, the total amount of time required for one titration cycle using a 0.1 ml AEA dose was typically 72.5 s, although this can be much smaller or larger.

2.3. Surface tension tests

Surface tension measurements with deionized water containing SDBS and VR and fly ash–water mixtures containing VR were accomplished. A rather simple approach was used that relied on measuring the force needed to pull an immersed needle from the mixtures as the amount of titrated AEA was increased [24]. Both AEA's were titrated into 200 ml of water with or without 80 g of fly ash. Prior to testing, the AEA's were diluted 100:1 (water:AEA) for water surface tension testing whereas the AEA was diluted 4:1 (water:AEA) for water–fly ash surface tension testing.

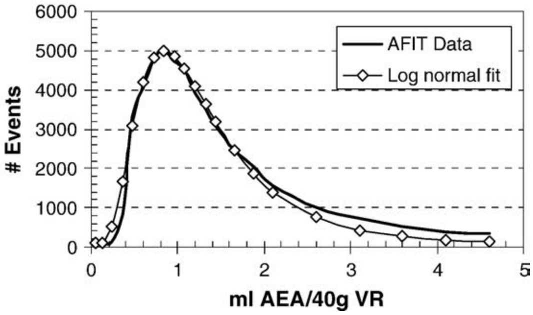

Fig. 3. A foam index curve acquired using the AFIT instrument on Ash2 and a Log normal fit to experimental data (see Section 3.5).

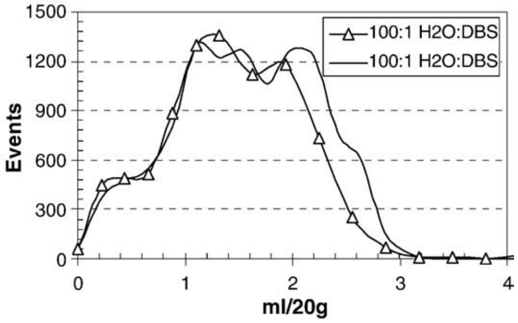

Fig. 4. AFIT data from Ash10 when using DBS as the AEA.

The force needed to pull the immersed needle out from either the water or water–fly ash samples without AEA was measured. The AEA was then titrated into the liquid, followed by complete mixing for 2–3 min without creating surface bubbles, and then the mixture was allowed to equilibrate for 2–3 min before the force needed to pull the needle out was again measured. Up to 15 titration steps were performed during each test. Because the absolute value of the force for water–fly ash mixtures was affected by ash particles floating on top of the water and which were attached to the needle as it was pulled from the mixtures, reported herein are relative surface tension values, i.e. force after AEA titration divided by the force when no AEA was present.

2.4. ASTM C231 testing

Air content measurements of freshly mixed concrete followed the ASTM C-231 standard [25] while using a Type B concrete air meter (Gilson Company, Inc). Portland cement (Type I/II) and All Purpose Sand and Gravel (meeting ASTM C-33 specifications) were acquired from a local retail establishment. Mixtures of these components with and without combustion fly ash were made while using a ratio (cement plus ash)/water = 1.77. These mixtures were placed in the concrete air meter and air contents measured, establishing average air content values from three individual tests.

3. Results and discussion

3.1. AFIT data repeatability

Representative AE results during two successive acoustic data acquisition tests are shown in Figs. 4 and 5 for two different fly ashes having different sample masses. For the Ash10 data in Fig. 4, SDBS was diluted in a ratio water:AEA = 100:1; for the Ash8 data in Fig. 5, MA was diluted in a ratio water:AEA = 4:1. The abscissa in each graph is a ratio (ml AEA plus water)/g ash and the ordinate in each plot is Events, i.e. the number of bubbles bursting during a 45 second AE detection period. Excellent repeatability in the number of acoustic Events is noted during each data collection period as the AEA titration levels were increased. Besides the amounts of AEA required to attain the foam index values, a primary difference between these AE AFIT data is the peak number of Events: in Fig. 4 the maximum is near 1350 Events whereas it is only 160 Events in Fig. 5. Differences in the maximum number of Events are commonly found, and are related to AEA type and dilution, titration dosage levels, sample type and LOI level, and sensor signal amplification. Repeatability of foam index values of individual ashes tested to date has been ± 14% (± 2σ).

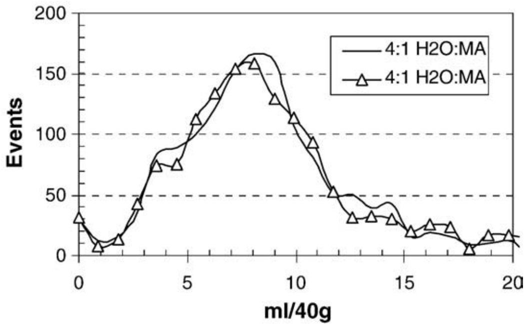

Fig. 5. AFIT data from Ash8 when using MA as the AEA.

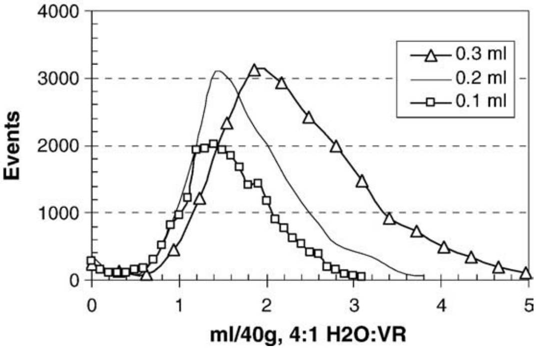

Fig. 6. Foam index curves for Ash2 with varied AEA titration levels.

3.2. Dynamics of AEA uptake

Fig. 6 displays three AFIT curves for Ash2 while using AEA titration levels between 0.1 and 0.3 ml. The peak curve positions were identical when 0.1 ml and 0.2 ml titration doses were used whereas the peak was shifted to a higher value when using 0.3 ml titration doses. Table 3 presents the foam index values from the peak position of these curves: they were 1.4 ml/40 g of ash, or 0.28 ml AEA/40 g of ash, when 0.1 and 0.2 ml titration doses were used; and 2.0 ml/40 g, or 0.4 ml AEA/40 g of ash, when a 0.3 ml titration dose was used.

Also displayed in Table 3 is the total time taken to measure the foam index values. Even though the overall measurement time (511 s) to reach 1.4 ml/40 g when using 0.2 ml doses was less than 1/2 of the time (1015 s) when using 0.1 ml doses, the constant foam index values points to achieving equilibration in AEA absorption by ~511 s after beginning the measurement. When using 0.3 ml doses the time needed (514.5 s) to achieve the 2.0 ml/40 g foam index value was very close to the time needed during the 0.2 ml titration test to achieve 1.4 ml/50 g; furthermore, when using 0.3 ml doses the time needed (367.5 s) to achieve an accumulated AEA dosage of 1.4 ml/40 g was significantly less than the time needed during 0.1 and 0.2 ml titration tests. Hence, these data suggest the equilibration time for VR absorption onto Ash2 was greater than 367.5 s but less than 511 s; they also point to an ability to measure AEA absorption dynamics by use of the AFIT instrument.

Another approach to studying equilibration times is to change the level of a preliminary dose relative to those of subsequent titration steps. This approach was used for determining AEA equilibration on

Table 3
Dose, foam index values and equilibration times during VR titration onto Ash2.

Sample	Dose level ml	Foam index value, ml/40 g	Pure AEA value, ml/40 g	Time, s, to attain value	Time, s, to 1.4 ml/40 g
Ash2 4:1 water:VR	0.1	1.4	0.28	1015.0	1015.0
	0.2	1.4	0.28	511.0	511.0
	0.3	2.0	0.40	514.5	367.5

Table 4
Dosages, index values and equilibration times during VR titration onto Ash1.

Sample	Dose level ml	Foam index value, ml/40 g	Pure AEA value, ml/40 g	Time, s, to attain value	Time, s, to 1.55 ml/40 g
Ash1 1:1	0.05	1.54	0.77	2166.5	2166.5
water:VR	0.1	1.57	0.78	1138.3	1138.3
	0.8 then 0.1	1.78	0.89	786.5	634.3
	1.2 then 0.1	1.86	0.93	556.5	346.3

Ash1 (Table 4). The foam index value was constant between 1.54 and 1.57 ml/40 g of ash, or 0.77–0.78 ml AEA/40 g, when no preliminary dose was applied and either 0.05 ml or 0.1 ml per titration was used throughout the testing. When a 0.8 ml preliminary dose was applied and then 0.1 ml per doses were used in all subsequent steps, the foam index value increased to 1.78 ml/40 g of ash, or 0.89 g AEA/40 g. Increasing the preliminary dose to 1.2 ml further increased the foam index value to 1.86 ml/40 g of ash, or 0.93 ml AEA/40 g. Hence, the equilibration time for Ash1 was between 786.5 and 1138.3 s (13.1–19.0 min), about two times greater than the equilibration time for Ash2. That the foam index values were increased instead of decreased when a larger initial dose of either 0.8 or 1.2 ml was used, or as stated in reference [20] — when there was a “quick addition of a large amount of AEA”, is expected to be a consequence of differences in data acquisition herein relative to those used in visual techniques. For example, visual observation monitors only the surface of a mixture that can accumulate a thick and seemingly stable foam layer during the time of observation whereas the AFIT method detects both surface and subsurface Events that will be high before AEA equilibration and site saturation occurs. Hence, a consequence of “quick addition of a large amount of AEA” is to shift AFIT peaks to AEA titration levels higher than would otherwise define the actual foam index values.

3.3. Changing water:AEA dilutions

The dilution of the AEA was different for the data presented in Tables 3 and 4. To determine whether foam index values were dependent on or independent of AEA dilutions used, a series of tests were performed using dilution ratios of 2:1 water:MA and 4:1 water:MA. In Fig. 7 are displayed the foam index curves for Ash9 using these dilution ratios; the dashed vertical lines within the plots signify the peak of the foam index Events. For 2:1 dilution the foam index was 27.5 ml/20 g; for 4:1 dilution the foam index was 45 ml/20 g. The ratio of the diluted AEA between these two tests was 2:1/4:1 = 3/5 = 0.6; the ratio of the foam index values was 0.61. Hence, foam index values were independent of AEA dilution as long as equilibration for adsorption onto the solid sites was met.

Table 5 presents foam index values for cement–Ash1 mixtures when using different water:VR dilutions. By plotting the foam index values for 4:1 and 2:1 dilutions relative to the 1:1 values, as displayed in Fig. 8 for Ash1 and Fig. 9 for Ash2, it was possible to determine whether diluting the AEA affected the absolute foam index values based on ml of pure AEA and whether the equilibration times discussed in Tables 3 and 4 were affected by AEA dilution. In both figures the abscissa represents the foam index for 1:1 VR and the ordinate represents the foam index in ml of solution for more highly diluted VR.

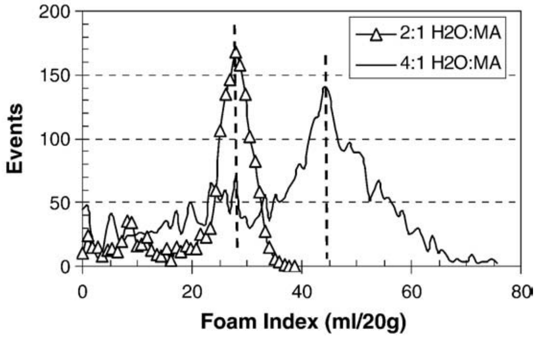

Fig. 7. Foam index curves for Ash9 when different AEA dilutions were used.

Table 5
Foam index values (ml AEA + water/40 g of sample) for cement–Ash1 mixtures using different dilutions of water:VR.

	VR dilution		
% Ash1	4:1	2:1	1:1
100		3.80	2.55
80	2.10	1.10	0.80
50	1.13	0.70	0.60
30	0.70	0.60	0.50
20			0.30
0	0.5		0.16

The linear fits to data in Fig. 8 have slopes of 1.57 for 2:1 H_2O:VR and 2.42 for 4:1 H_2O:VR. If foam index values were independent of the dilution the theoretical slope values would be 1.5 and 2.5, respectively. Similarly, the linear fit to Ash2 data in Fig. 9 had a slope of 2.84 for 4:1 H_2O:VR whereas the theoretical slope value should have been 2.5, i.e. 13.6% smaller than the actual value. In other words, foam index values calculated on the basis of the amount of pure AEA were independent of the dilution of the AEA that was used during titration. As a consequence, the AEA equilibration times discussed for Ash1 and Ash2 in Tables 3 and 4 were not affected by having used different water:AEA dilutions.

This outcome provides greater flexibility in acquiring AFIT data especially for samples that have either very low propensities to absorb AEA, like cement or some pozzolans, or very high propensities to absorb AEA, like ashes with high LOI's or with very active AEA absorption. In the former, the establishment of high-quality and low-noise foam index data can be accomplished by highly diluting the AEA before data acquisition. In the latter, the time required to obtain data could be decreased by using less dilute AEA — as long as equilibration of the AEA is accomplished. Importantly, these types of data acquisition modes must account for aging of the AEA that may occur, an expression of which is a slowly increasing peak position within the foam index curve for a sample and very similar to the difference observed in Fig. 6 when AEA solid equilibration times were not fully met.

3.4. Surface tension

In Fig. 10 are presented relative surface tension data for water upon titrating SDBS and VR along with a ±2σ repeatability bar for each data

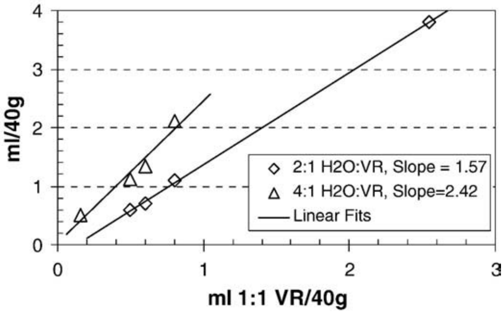

Fig. 8. Comparison of foam index values for cement–Ash1 mixtures for 1:1 H_2O:VR relative to 2:1 and 4:1 dilutions.

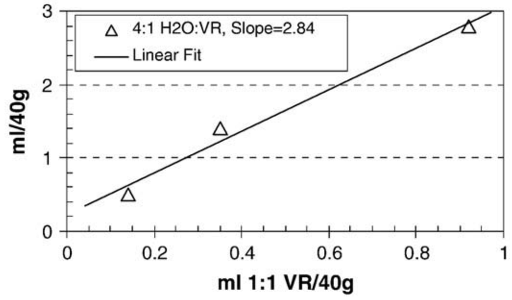

Fig. 9. Comparison of foam index values for cement–Ash2 mixtures for 1:1 H_2O:VR relative to 4:1 dilution.

set. An initial rapid decline in the relative surface tension is followed by a plateau in which very small decreases occurred. Taking 0.1 ml AEA as the point of achieving a critical micelle concentration (CMC) gives the CMC concentration as 0.47 g/l for both SDBS and VR; previous data for SDBS in water has determined CMC values between 0.24 and 1.82 g/l [22].

Fig. 11 compares AFIT data with relative surface tension data when VR was titrated into water. The number of AE Events began to increase and the relative surface tension began to decrease immediately upon titrating VR. Relative surface tension values as well as the number of AE Events began to level near 0.1 ml VR. Upon reaching the estimated CMC value of 0.1 ml AEA, the AE signal had decreased to less 1/8 of the maximum number of Events.

Fig. 12 compares AFIT AE data with relative surface tension data when VR was titrated into water–fly ash mixtures. In agreement with the Fig. 11 data for water only: the number of AE Events began to increase as the liquid surface tension began to decrease; the number of Events went through a maximum as the surface tension was decreasing; the number of Events decreased to lower values and then leveled concomitant with a leveling in the relative surface tension. Therefore, the rise and decrease in AE Events from water and water–ash mixtures as AEA is titrated into the mixture can be associated with a decrease in surface tension of the liquid layer and the eventual attainment of CMC levels.

3.5. Mathematical derivation of foam index-surface tension correlations

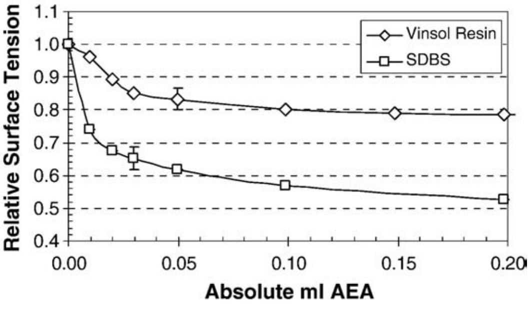

Fig. 10. Relative surface tension values in water after titration of VR and SDBS. The $\pm 2\sigma$ error bar in the surface tension data represents the general repeatability of the data.

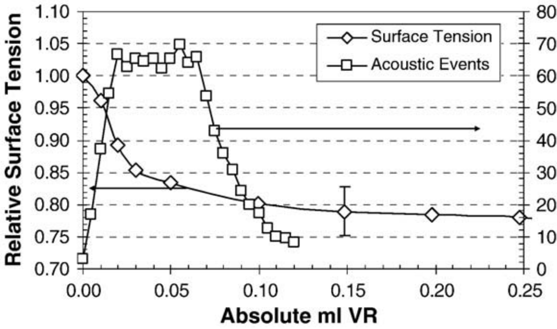

Fig. 11. Relative surface tension of and AE Events from VR-water mixtures. The $\pm 2\sigma$ error bar in the surface tension data represents the general repeatability of the data.

A relationship between the surface tension, ST, and surfactant concentrations, C, in liquid solutions discussed by Acharya, et al. [26] showed a linear relationship between ST and C when formulated in a semi-logarithmic manner as long as C was below CMC. At concentrations greater than CMC, the ST values become constant because the clustering of the surfactant into micelles produces equilibrium between the free molecules and micelles in solution. Therefore, a mathematical model can be derived that takes into account this behaviour by taking ST_{max} as the maximum surface tension value corresponding to the lowest amount of AEA used during the tests, C_{min}, and ST_{min} — or ST_{CMC} — as the minimum surface tension corresponding to the Critical Micelle Concentration (CMC), and can be expressed as:

$$\frac{ST - ST_{max}}{\log(C) - \log(C_{min})} = \frac{ST_{max} - ST_{min}}{\log(C_{min}) - \log(CMC)} \tag{1}$$

So:

$$ST = ST_{max} - \frac{ST_{max} - ST_{min}}{\log\left(\frac{CMC}{C_{min}}\right)} \cdot \log\left(\frac{C}{C_{min}}\right). \tag{2}$$

This mathematical construct provides a way to describe surface tension behavior upon changing the surfactant concentrations, as presented in Fig. 13; it is compared to the "experimental" surface tension data from water using SDBS. Although the shape of the curves is similar, there are substantial differences between the simulation and experimental data to suggest additional influences not considered by the simulation. One of these may be the surface tension data that was obtained by the needle immersion method: as could be expected, cenospheres were the dominant form of the ash floating on the water's surface and it was observed that the amount of cenospheres clinging to the needle as it was pulled out of the ash–water mixtures was less at low AEA titration levels than at high AEA levels. This difference could have increased needle buoyancy at high AEA levels, which in turn would change the extent to which the measured surface tension decreased as the amount of titrated AEA increased.

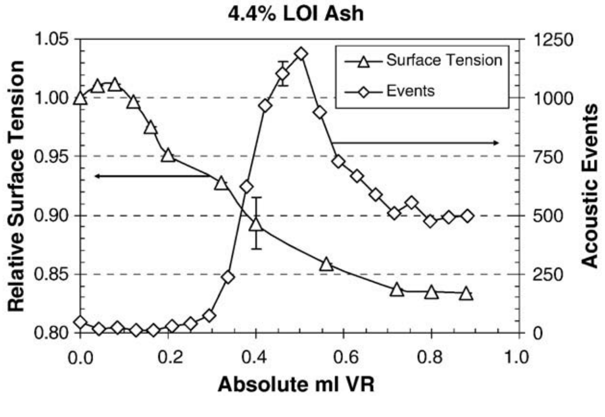

Fig. 12. Relative surface tension of and AE Events from water–fly ash mixtures. The $\pm 2\sigma$ error bar in the surface tension data represents the general repeatability of the data.

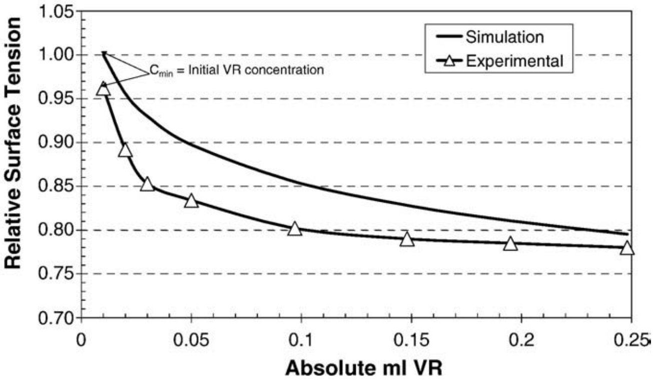

Fig. 13. Comparison of simulated and experimental surface tension trends with VR titrated into water.

It was determined that typical shapes of AFIT curves, as shown in Fig. 3, could be well-represented using a exponential, log-normal fit having the following form:

$$A = A_{\max} \ + \ ae^{-[\log(A/Ao)/b]}, \tag{3}$$

where $A_{\max}$ is the maximum number of Events measured by the AFIT instrument, A_o is the number of AE Events measured after water is added but before AEA is added to the sample, and a and b are fitting parameters. Hence, to examine a potential relationship between AFIT curves and surface tension data, an exponential expression was used as the mathematical relationship between surface tension and number of measured Events, A:

$$A = A_{\max} \cdot \ \exp\left[-\frac{(\mathrm{ST} - \mathrm{ST}_{\min})}{\tau}\right] \tag{4}$$

where τ is the whole range of surface tension divided by an integer fitting parameter, n,

$$\tau = (\mathrm{ST}_{\max} - \mathrm{ST}_{\min})/n, \tag{5}$$

and $A_{\max}$ is the maximum amount of bubbles created. Combining Eqs. (4) and (5) gives:

$$A = A_{\max} \cdot \ exp\left[-(\mathrm{ST} - \mathrm{ST}_{\min}) \cdot \left(\frac{\mathrm{ST}_{\max} - \mathrm{ST}_{\min}}{n}\right)^{-1}\right]. \tag{6}$$

Hence, the dimensionless number of bubbles, $A/A_{\max}$, depends only on surface tension values and the fitting parameter, n.

The initial increase of the AE observed in Figs. 11 and 12 is consistent with Eq. (6) but the extent of the plateau region is not represented by this construct: for example, the AFIT data in Fig. 11 could be fitted only by assuming a CMC of about 0.02 rather than the ~0.1 value obtained from the surface tension tests. Oppositely, the number of AE Events and surface tension values were constant beyond an AEA concentration of ~0.8 in Fig. 12 and Eq. (6) could be used to represent this behavior. Therefore, although the representation given in Eq. (6) explains some of the AFIT data, it is suggested that a more robust theoretical approach may be needed or additional considerations need to be considered that affect bubble stability and surface tension.

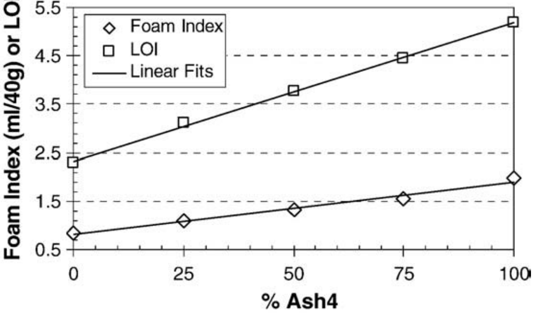

Fig. 14. Foam index values from AFIT and LOI's of Ash3–Ash4 mixtures.

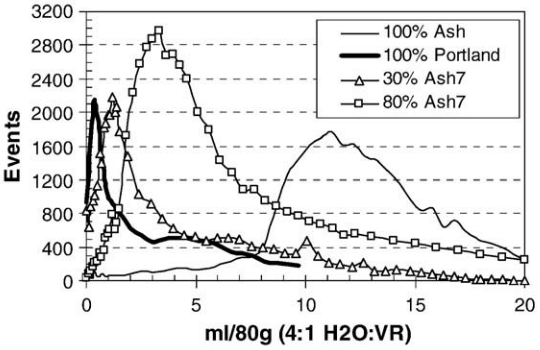

Fig. 15. Foam index curves for cement–Ash7 mixtures.

One possibility that is succinctly described in a report from the National Highway Research Program (NCHRP) [27] relates the stabilization of bubbles in concrete to three events: first, the surface tension is lowered; second, the adsorbed AEA molecules at the surface of a bubble form a film, with the polar head in the water phase; and third, the ends of the AEA molecules that protrude into the water are attracted to cement grains, allowing for the formation of a coating of calcium salts (i.e. products of cement hydration) around each air bubble making it more stable than bubbles formed in plain water. This type of dual reactivity, i.e. surface tension and interactions with free calcia, would affect bubble stability and the concomitant acoustic signals measured in the liquid layer using the AFIT method. Furthermore, as discussed by Grau et al. [28], the size of bubbles can be expected to change during surfactant titrations, and become constant when the level of the surfactant attains a value they called the Critical Coalescence Concentration. As the bubble size changed, their eventual bursting would be expected to change both the intensity and frequency of the AE measured in our tests. Although it is possible to perform Fourier transform (FT) analyses on the time domain AE data that were collected (as represented in Fig. 1), and although preliminary FT analyses have shown the AE frequencies to increase as AEA titration levels were increased, this aspect of foam behavior has not been assessed to a degree that points to an affirmative conclusion.

3.6. AFIT data of cement, fly ashes and cement–ash mixtures

Fig. 14 shows that foam index values of 100% Ash3, 100% Ash4 and mixtures of Ash3 and Ash4 samples were linearly related, and linearly increased with increasing LOI contents as the percentage of Ash4 attained the 100% level. Linearity in foam index values with increasing LOI values suggest that the carbon content in the Ash3–Ash4 mixtures controlled their foam index values. The potential of assessing factors

Table 6
Measured and calculated foam index values for cement–ash mixtures: calculated values assume that carbon contents would control AEA uptake.

Sample	LOI content %	Measured foam index, ml/80 g	Calc. foam index, ml/80 g, from LOI
100% cement	0.10	0.6	
70% cement:30% Ash7	1.17	1.5	3.6
20% cement:80% Ash7	3.12	4.1	9.6
100% ash	3.90	12.1	

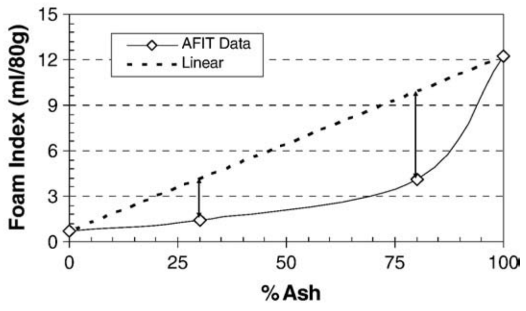

Fig. 16. Foam index values of cement–Ash7 mixtures.

other than the content of carbon that may control foam index values was then examined by testing cement–ash mixtures.

Fig. 15 displays AFIT foam index curves for 100% Ash 11, 100% Portland cement and mixtures of Ash7-cement. Portland cement absorbed considerably less AEA than did Ash 11. In fact, to display a fully developed foam index curves as depicted in Fig. 15 for a sample having a very low foam index value it can be necessary to either decrease the AEA dosage rate (0.1 ml per dose was used during AFIT data collection for Fig. 15) or to increase the dilution of the AEA (4:1 H_2O:VR was used during AFIT data collection for Fig. 15). As seen in Table 6 and in Fig. 16, the foam index values of cement–ash mixtures could not be represented by linear extrapolated values calculated by the two endpoints, 100% cement and 100% ash. Because the amount and type of carbon would increase proportionally with the percentage of ash in the cement–ash mixtures, whereas the foam index values did not increase in the same proportion, it is proposed that components other than carbon and interactions other than with carbon — as are discussed in references [15–17,20] — also influence the foam index values. This conclusion is also in agreement with that from the preceding assessment of the mathematical construct relative to foam index and surface tension data. In other words, significant cement–ash chemical interactions occur that are reflected in the AFIT data.

Although the presence of Ca^{2+} and Mg^{2+} specie have been proposed to diminish AEA foaming in cement–ash mixtures [20], their contribution would be primarily dependent on the cement content in the mixtures examined. Because the foam index value of 100% cement was more than 20 times less than of 100% Ash7, it is expected that the influence of Ca^{2+} or Mg^{2+} species in this sample on AEA uptake was small relative to the influence of carbon. Hence, some form of cement–ash interaction had to occur to diminish the effect of carbon on AEA uptake in some cement–ash mixtures, as is displayed in Figs. 16 and 17. The possible form(s) of these interactions were not investigated.

Figs. 16 and 17 show foam index values of cement–ash mixtures were widely variable relative to the amount of ash in the mixtures and, generally, could not be expected to be linearly dependent on the LOI, or ash, content of the mixture. In Fig. 17 a parameter called the relative foam index values is plotted as the ordinate graph value — the foam index value for each mixture divided by the foam index value at 100% ash — because the absolute foam index values were widely different. The behavior observed for cement–Ash5 and cement–Ash6 mixtures were similar to those measured for cement:Ash7 mixtures, i.e. values were less than a linear representation would have predicted as the ash concentrations were increased. However, foam index values of cement–Ash2 mixtures were linearly dependent on the ash concentrations and foam index values of cement–Ash10 mixtures were greater than a linear representation would have predicted. The overall practical effect of these AFIT data points to the need to use cement–ash mixtures rather than just ash by itself during foam index testing if the effect of the ash on AEA uptake in cement–ash mixtures is to be obtained. Furthermore, the capability to measure foam index values independent of user bias and to follow the dynamics of AEA uptake was seen to offer an approach to potentially measure the amount of AEA required to control air content specifications within concrete mixes.

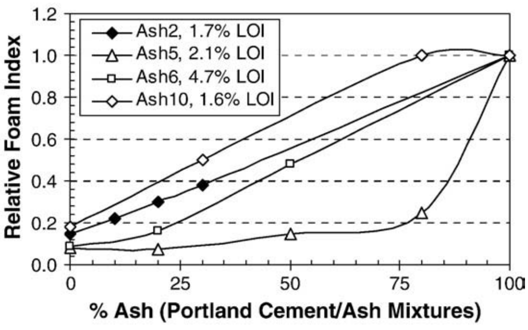

Fig. 17. Relative foam index values of four different cement–ash mixtures.

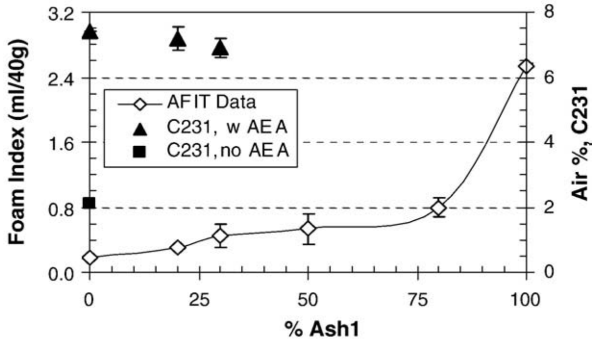

Fig. 18. Foam index values and C231 air contents of cement–Ash1 mixtures.

3.7. AFIT foam index values and C231 data

As noted by Baltrus, et al. [20], it may be possible to lower the adsorption capacity of cement for an AEA by substituting an ash that replaces or interacts with free Ca^{2+} and Mg^{2+} from the cement. This statement was based on visual foam index and UV–Vis data that concluded the presence of these free ions was more important in AEA uptake than the presence of unburned carbon, whereas other publications have focused on the role of unburned carbon [15–18]. From the data in Figs. 16 and 17 it is obvious that foam index values of cement–ash mixtures do not always increase linearly with increasing fly ash content and that some form of cement–ash interaction may influence AEA uptake in addition to absorption of AEA by unburned carbon.

To further examine the practical effects of such behavior, AFIT derived foam index values in cement–ash mixtures were used to determine the amount of AEA to be added to concrete mixes, and then these mixes were subjected to measurement by using the ASTM C231

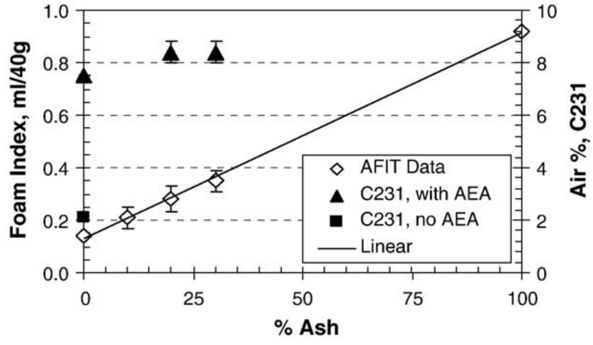

Fig. 19. Foam index values and C231 air contents of cement–Ash2 mixtures.

air content method [25]. Shown in Fig. 18, the C231-determined air contents for cement–Ash1 mixtures using 0%, 20% and 30% fly ash were approximately constant at 7.4%, 7.2% and 6.9%, respectively; also shown is the air content of a concrete mix without AEA added. If the amount of AEA added had been estimated to be linearly dependent on Ash1 content instead of from measured foam index values, the amount of AEA used for the 20% and 30% admixtures would have been ~2 times larger than the values actually used, leading to significantly greater concrete mix air contents. For cement–Ash2 mixtures (Fig. 19), the amount of AEA to be added by AFIT measurements was determined to increase linearly with ash concentration. Consequently, the concomitant C231 air contents were found to be approximately constant at 7.4%, 8.4% and 8.4%, respectively. Hence, the AFIT method made it possible to instill constant air contents in the mixtures. It also provides a convenient approach to quantitatively measure the AEA dosage at which air bubbles become stabilized within concrete mixtures independent of the extent to which unburned carbon, free alkali ions or other cement–ash interactions control or significantly influence AEA uptake.

4. Conclusions

Automation of the foam index test was accomplished by detecting acoustic waves emanating from a container in which cement–ash mixtures were placed and into which water was added, AEA was dosed and sample agitation was performed using precise computer control. The real-time nature of the acoustic emission from this AFIT instrument provided dynamic assessments of foam stabilities for ash and cement–ash mixtures even with different AEA's. Shapes of the AFIT curves as a function of increasing AEA dosages were experimentally correlated with changes in liquid surface tensions and were mathematically assessed to depend on other factors in addition to surface tension. These interactions were independent of the AEA dilution used during the AFIT testing as long as AEA equilibration with solid adsorption sites was met. It was also possible to measure dynamic adsorption and equilibration of AEA onto the cement and ash surfaces. These data suggest previous discussions about the relative importance of unburned carbon versus free Ca^{2+} and Mg^{2+} surface sites on AEA uptake is ash dependent and not exclusive to either carbon or free ions independent of each other. Nevertheless, it was possible to instill constant wet concrete air contents when substituting up to 30% ash for cement in concrete mixes if the AFIT determined foam index values were used as the measure for the amount of AEA to be added to the concrete mixes. Overall, AFIT operation instilled quantitative foam index measurements independent of the type of AEA or the types of ashes used during testing.

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