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Hydration and Air Entrainment Challenges of High-Volume Fly Ash Concrete Pavement

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The goal of high-volume fly ash concrete (HVFA) is to produce concrete pavements at a lower cost and carbon footprint while maintaining its desired durability. Previous research has demonstrated that the required fresh and hardened concrete properties can be achieved at higher replacement rates of cement with fly ash such as 40%. However, most transportation agencies do not permit more than 30% cement replacement with fly ash primarily because of the potential inconsistencies in early-age properties such as variable air entrainment, delays in setting times, and lower strength gains. In this paper, the heat evolved during hydration of HVFA are presented with respect to the source of the cement and fly ash, the variability of fly ash from the same source, and addition of nano limestone. Isothermal calorimetry showed longer setting times were dependent on the specific fly ash-cement combination as well as the degree of sulfate imbalance. For this study, HVFA mixes with class C fly ash had a larger sulfate imbalance than class F fly ash with final setting times 4.5 hours and 1.9 hours longer than straight cement system, respectively. Replacing cement with 10% nano limestone in HVFA system accelerated the initial set time by 3.2 hours which was much greater than the set time acceleration (1.3 hours) with the replacement of straight cement with 10% nano limestone. The various types of inorganic and organic carbons in fly ash remain a challenge for predicting and maintaining air content but the foam index still offers a rapid and straightforward quality control test with operator variability within $\pm 1 \mu\text{L}$ AEA/gm fly ash.

Sulfate Imbalance | Air Entrainment | Setting Time | Nano Limestone | Fly Ash

1. INTRODUCTION

Replacing cement with fly ash has been practiced for decades with the primary objectives being to reduce the concrete material unit cost and increase material durability. More recently, improving the sustainability of concrete has encouraged discussion on even higher replacement levels of cement with fly ash. Some of the specific performance benefits of partial replacement of cement with fly ash are mitigation of alkali-silica reaction (Detwiler, 1997), decreasing ion permeability (Yurdakul et al., 2014), improving salt-scaling resistance and reducing joint deterioration susceptibility (Farnam et al., 2017; Suraneni et al., 2017), and lowering the heat of hydration of mass concrete (Bamforth, 1980). Although many advantages exist for higher volume fly ash concrete mixtures, early-age properties such as air content, setting times, and strength gain rates can be affected (Taylor et al., 2006a), which can limit the permissible replacement levels.

The influence of fly ash on the concrete early-age properties depends on chemical composition of crystalline and amorphous phases, volume replacement level, and particle size. Restrictions on fly ash use based on broad oxide contents or arbitrary

replacement levels can lead to missed opportunities, which can improve both the cost and durability of concrete pavements. Furthermore, the discussion of non-compliance fly ash applications in concrete is gaining attention in the United States with many agencies seeking solutions to reclaim old fly ash ponds and stockpiles that may be contributing to downstream pollution or health risks.

With the urgency to apply higher replacement levels of fly ash in concrete pavements, rapid advanced characterization techniques of the fly ash coupled with mineral and chemical admixtures can provide the appropriate testing protocols and mixture modifications to enable use of High Volume Fly Ash Concrete (HVFA), i.e., cement replacement rates of 40% or higher. The use of HVFA is particularly challenging in cold climates because of lower set times, lower strength gains and a higher risk of plastic shrinkage. Additionally, variability of fly ash obtained from the same source over time generally requires diligent quality control. This paper investigates the heat evolved for a variety of cement-fly ash sources and replacement levels as well as quarterly variation of fly ash from the same source. Moreover, the addition of nano-limestone on heat evolution and set time acceleration is also presented. Finally, the potential impact of fly ash sources on air-entrainment performance are discussed along with the robustness of the foam index test.

2. HYDRATION REACTION

The application of 40% or higher replacement levels of cement with fly ash will affect the fresh and hardened properties of concrete. The degree to which it affects the HVFA properties will depend mainly on the chemical composition of amorphous and crystalline phases, and particle sizes of the cement-fly ash blend. Coupling the hydration reactions and heat evolution with the chemical compositions of the cement-fly ash blend can provide insight into strategies to achieve setting times and strength gains more similar to 100% Portland cement or lower volume fly ash mixtures. Fly ash generally has a higher Al_2O_3 and SiO_2 and lower CaO content than typical cement. Moreover, fly ash also has significant amount of amorphous aluminosilicate phases that take part in pozzolanic reaction in the later stages of hydration. Some fly ash may also contain non-reactive materials like carbon and quartz. HVFA may also have an increased tricalcium aluminate to sulfate ratio leading to sulfate imbalance (Thomas, 2007) and variable setting times depending on the fly ash content and cement source. Sulfate imbalance and application of nano limestone to

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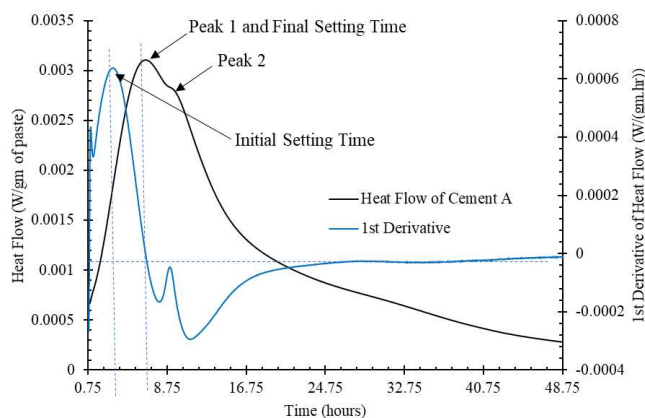


Fig. 1. Isothermal calorimetry results for Portland Cement A with initial and final setting time of 3.3 hours and 6.5 hours, respectively.

accelerate the initial setting time are discussed in the next two sections with respect to isothermal calorimetry test results.

A. Sulfate Imbalance. In Portland cement, calcium sulfate, generally in the form of gypsum, is added to delay the hydration rate of tricalcium aluminate (C_3A) (Minard et al., 2007; Quennoz and Scrivner, 2012). Calcium sulfate also influences the tricalcium silicate hydration rate as calcium silicate hydrate precipitation is accelerated with the abundance of Ca^{2+} ions dissolving from calcium sulfate (Li et al., 2019). In general, fly ash has a negligible amount of calcium sulfate present, but it may have a significant amount of C_3A , especially in class C fly ash. Thus, HVFAC reaction kinetics, setting time, and strength gain can vary significantly with the specific cement-fly ash interaction.

Isothermal calorimetry is a convenient tool to detect whether the cement-fly ash system is properly sulfated. Figure 1 shows a typical heat flow versus time curve normalized to the mass of paste obtained from a calorimeter test of Portland Cement A. In this paper, isothermal calorimetry was performed at $22^\circ C$ with the initial 45 minutes excluded because of the time required for calorimeter stabilization after sample insertion. For the Cement A test in Figure 1, Peak 1 represents the alite (C_3S) hydration peak, Peak 2 is the secondary ettringite formation, and the small valley between Peak 1 and Peak 2 is called sulfate depletion point (Bullard et al., 2011). The relative closeness and position of Peak 1 and Peak 2 of pure cement indicates a well-sulfated system. When the peaks are extremely close to each other or merged, the system is considered optimally sulfated.

Isothermal calorimetry can also be used to predict the trends in the initial and final setting times. As shown in Figure 1, the initial inflection point of the heat flow curve (2nd derivative set to zero) is defined as the initial setting time, whereas Peak 1, the C_3S hydration peak, is defined as the final setting time (Hu et al., 2014). The lesser amount of gypsum present in the under-sulfated system lowers the amount of Ca^{2+} dissolving from gypsum which in turn decreases the C-S-H precipitation rate and delays the C_3S peak hydration rate. Thus, under-sulfated systems have a longer final setting time compared to a well-sulfated system. The setting times obtained from calorimeter data should not be directly compared with the setting times obtained from ASTM C403 (2016) tests, but

the trends in setting time among different mixes observed from calorimeter data is similar to the trend observed from the standard ASTM tests (Hu et al., 2014).

Figure 2 shows calorimeter test data (heat flow normalized to the mass of paste versus time) for a blend of 40% fly ash and 60% Portland cement for two cement sources used in Illinois. The heat flow rates of the blended systems were lower than the 100% Portland cement system for the first 10 hours of hydration because C-S-H nucleation occurs during that time period. Since fly ash does not contain tricalcium silicate as the dominant phase, HVFAC produces lower C-S-H in the early period. In terms of sulfate imbalance, Cement B is considered a more well-sulfated system as compared to Cement A as Peak 1 and Peak 2 are closer for Cement B (Figure 2). Sulfate imbalance mostly occurs in HVFAC containing class C fly ash compared to class F fly ash because Class C has higher amount of C_3A than class F ash (Bentz, 2011), as observed in Figure 3. As discussed before, the final setting time delayed in under-sulfated system (See Figure 3a). For HVFAC mix with Cement A, the final setting time was delayed 2 hours by replacement with 40% class F fly ash (Figure 3b), but almost 4.5 hours for the same amount of class C fly ash (Figure 3a). Finally, the variation of the fly ash over a three-month period from the same source didn't significantly affect the measured heat flow as seen in Figure 3.

Chemical admixtures, especially the polycarboxylate-based high range water reducing admixtures, have been shown to affect the dissolution of gypsum, leading to more severe sulfate imbalance in under-sulfated systems (Pourchet et al., 2006; Taylor et al., 2006b) such as the case with HVFAC and class C fly ash (Bentz, 2011). Even though it is known that chemical admixtures affect the dissolution rate of calcium sulfates, there is limited research on how different types of chemical admixtures affect calcium sulfate dissolution rates (gypsum, hemihydrate, anhydrite) and potential sulfate imbalance. High volume fly ash replacement of cement are expected to further magnify chemical admixture interactions with cement-fly ash systems and thus, testing like isothermal calorimetry are important for the mix design process.

B. Effect of Nano Limestone Replacement. Nanomaterials offer a very high specific surface area and thus provide nucleation sites for calcium silicate hydrate precipitation. Nanomaterials that may be used to accelerate cement setting times include quartz, limestone, and TiO_2 . The effect of nano limestone replacement of Cement A on the heat flow curve is plotted in Figure 4. For all replacement levels of cement with nano limestone, the time to the initial peaks were reduced. Table 1 summarizes the decreased setting times when replacing cement with nano limestone, which has been reported by other researchers (Bentz, 2011). For 30% limestone replacement, the initial and the final setting times were accelerated by 2 and 2.6 hours, respectively. The heat flow measured after 20 hours of hydration decreased with increasing nano limestone content because of the dilution of cement in the total paste volume.

The next step was to determine if nano limestone replacement of cement with 40% fly ash could accelerate the setting times of HVFAC. The setting times were accelerated with increasing nano limestone addition for both class C and F ash mixtures. For 5% nano limestone addition in the HVFAC class C mix (Fly Ash 1), the initial and final setting times were accelerated by 2.6 and 2 hours, respectively, compared to 2 and

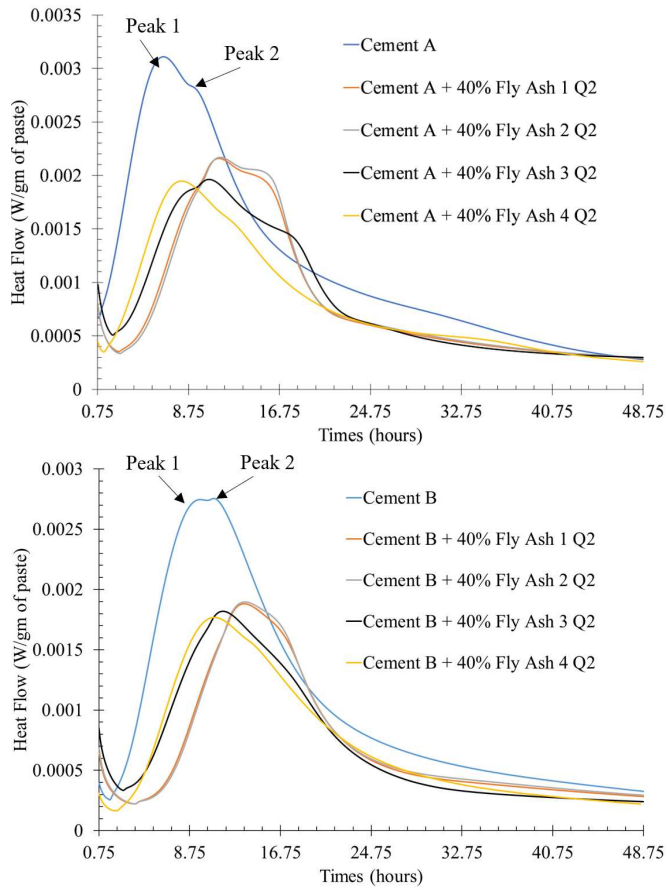


Fig. 2. Isothermal calorimetry results for (a) Cement A and (b) Cement B replaced with 40% class C (Fly Ash 1, Fly Ash 2, Fly Ash 3) and class F (Fly Ash 4) fly ash sources for 2019 quarter 2 samples (Q2).

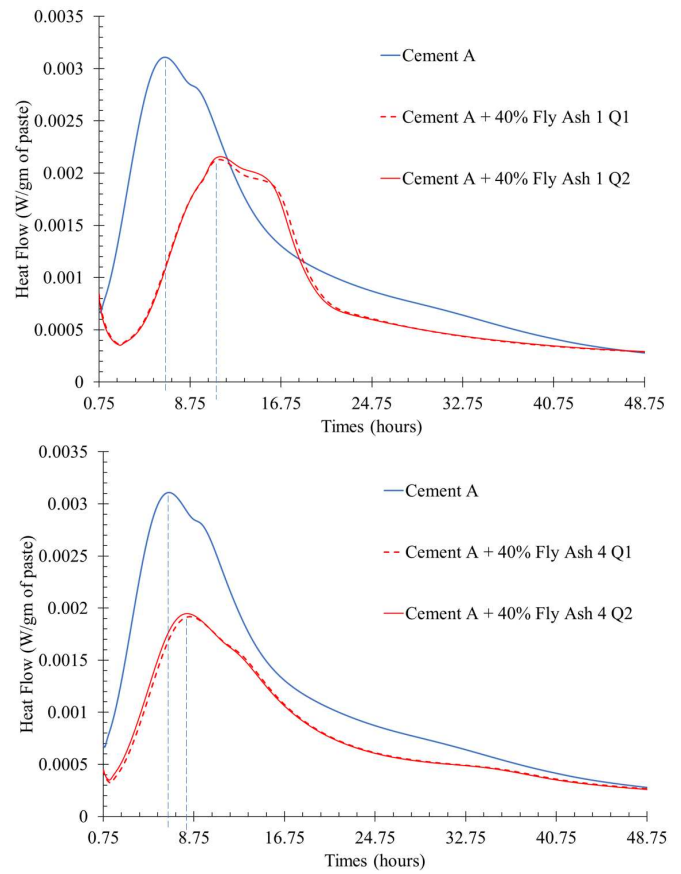


Fig. 3. Isothermal calorimetry results for 40% weight replacement of cement with (a) Fly Ash 1 (class C) and (b) Fly Ash 4 (class F) for two consecutive quarterly samples in 2019 (Q1 and Q2).

2.5 hours as observed in Bentz et al., (2012). Increasing nano limestone addition to 10% for Fly Ash 1 decreased the initial and final setting time by 3.2 and 2.7 hours, respectively. The set time acceleration was slightly lower for the system with 40% Fly Ash 4 (class F) and 10% nano limestone as initial and final setting times were 2.3 and 2.5 hours faster, respectively. In fact, nano limestone was more effective in accelerating setting time in HVFAC systems compared to straight cement systems. Replacement of Cement A with 10% nano limestone accelerated the initial and final setting times by only 1.3 and 1.8 hours, respectively.

In the case of class F fly ash replacement, the relative shape of peak 1 and peak 2 in the heat flow curve did not change significantly with nano limestone replacement of cement (See Figure 5b). However, for class C fly ash, the heat flow of peak 2 increases significantly compared to the heat flow of peak 1 when nano limestone replaced cement by more than 10% of total binder. Fly ash does not contain significant amount of calcium sulfate, but class C ash can have significant amount of tricalcium aluminates. In the samples tested in Figure 5a, nano limestone replaces the cement, but the amount of fly ash is kept constant. As a result, with increasing limestone replacement, the amount of calcium sulfate in the system decreases faster than the decrease in the amount of tricalcium aluminate, leading to a higher tricalcium aluminate to calcium sulfate ratio. This leads to the observed second peak having a higher intensity than the first peak in Figure 5a.

Even though nano limestone and limestone powder are considered filler material (Choudhary et al., 2016), they do affect the chemistry of the cement hydration products. In the 1960s, Feldman et al., (1965) showed that limestone affects the initial hydration reaction of tricalcium aluminate through a rapid formation of hydrated calcium carboaluminate formed on the tricalcium aluminate surface, which slows down the dissolution of tricalcium aluminate. Bonavetti et al., (2001) showed that calcium monocarboaluminate could be detected within 3 days of hydration. The amount of calcium monocarboaluminate increased after 28 days of hydration compared to 3 days of hydration mainly because of the conversion of calcium monosulfoaluminate to calcium monocarboaluminate. Presently, no literature is available on the effect of nano limestone on the hydrated reaction products in high volume fly ash concrete, but the initial data from the calorimeter tests suggest a modest cement replacement with limestone (e.g., 5% to 10%) or other nanoparticles should significantly accelerate the HVFAC setting times.

3. AIR ENTRAINMENT

Two-thirds of concrete in the United States is air-entrained for freeze-thaw durability (Dolch, 1996). Air entrained concrete has well-distributed, small air bubbles that relieve the hydrostatic stress developed during ice formation. The concrete mixing process generates the air bubbles in the paste, which may not be stable depending on the density and surface tension of the paste, the air bubble radius, and the hydrostatic pressure on the air bubble (Du and Folliard, 2005; Nagi et al., 2007). AEA used in concrete typically decreases the surface tension by as much as 20 mN/m (Mielenz et al., 1958), which prevents smaller bubbles from coalescing (Şahin et al., 2017) as the pressure difference between them decreases with a decrease in the surface tension of the medium. Additionally, larger air

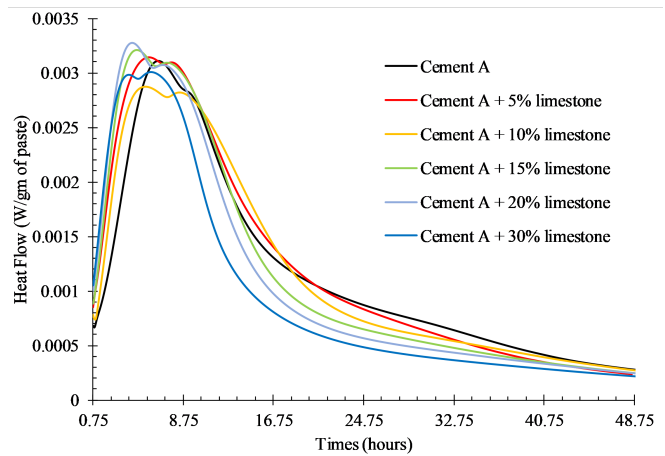


Fig. 4. Isothermal calorimetry results for Cement A and multiple weight replacement levels with nano limestone.

Table 1. Effect of nano limestone on the setting times of different binder blends. Fly Ashes 1 and 4 are class C and class F fly ashes, respectively.

Mix Name	Initial Setting Time (hr.)	Final Setting Time (hr.)
Cement A	3.3	6.5
Cement A + 5% limestone	1.8	5.8
Cement A + 10% limestone	2	4.7
Cement A + 15% limestone	1.9	4.6
Cement A + 20% limestone	1.7	4.2
Cement A + 30% limestone	1.3	3.9
Cement A + 40% Fly Ash 1 Q2	6.9	11
Cement A + 40% Fly Ash 1 Q2 + 5% limestone	4.3	9.0
Cement A + 40% Fly Ash 1 Q2 + 10% limestone	3.7	8.3
Cement A + 40% Fly Ash 4 Q2	4.7	8.4
Cement A + 40% Fly Ash 4 Q2 + 5% limestone	2.4	6.1
Cement A + 40% Fly Ash 4 Q2 + 10% limestone	2.4	5.9

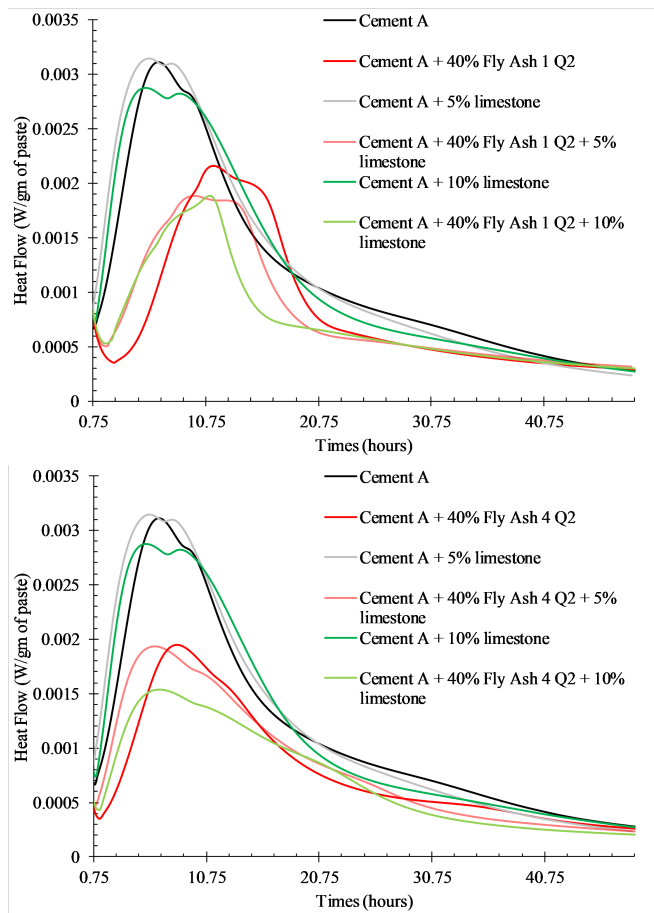


Fig. 5. Isothermal calorimetry results showing the effect of nano limestone replacement of cement in a system with 40% of the binder weight containing (a) Fly Ash 1 (class C) and (b) Fly Ash 4 (class F).

bubbles decrease compressive strength and are not effective in improving freeze-thaw resistance. Air-entraining admixtures are not equally effective in reducing surface tension of the medium. Ansari et al., (1999) showed synthetic resin for AEA in concrete produced larger air voids than Vinsol resin because of lower surface tension of Vinsol resin.

Air entrainment of high-volume fly ash concrete poses additional challenges for two main reasons. In general, the carbon content of fly ash has been increasing because of the introduction of low NO_x burners (Diaz-Loya et al., 2019). Additionally, use of powdered activated carbon for NO_x absorption also increases activated carbon content in fly ash. These carbon particles present in the fly ash provide a high surface area on which AEA can be adsorbed, and thus less AEA is available to stabilize the air bubbles. The Ca²⁺ and Mg²⁺ ions present in the paste may also cause the AEA to precipitate, which reduces the amount of available AEA. The types of carbon in fly ash and Ca²⁺ and Mg²⁺ ions present in the pore solution are discussed next with respect to its effect on air entrainment.

A. Types of Carbon in Fly Ash. The effect of carbon on air-entraining performance is well-documented with the ASTM C311 method (ASTM C311, 2018) created to limit the amount of carbon present in the fly ash through the Loss on Ignition (LOI) test. ASTM C618, (2019) limits the LOI to less than 6% for class C fly ash and LOI up to 12% for class F fly ash with air content performance test verification. However, the ASTM C311 LOI test overestimates the fly ash carbon content as the mass loss up to 750°C includes any bound water or other phases along with carbon.

The majority of researchers agree that air entrainment of fly ash concrete cannot be adequately predicted from the amount of carbon present in the system in bulk because the interaction of carbon and AEA depends on the different types of carbon (Freeman et al., 1997; Kūlaots et al., 2004). Carbon present in fly ash can be divided into organic and inorganic parts. It is generally accepted that only organic carbon takes part in AEA adsorption, whereas inorganic carbon is almost inactive (Pedersen et al., 2008). Multiple researchers (Chen et al., 2003, 2002; Gao et al., 2001) have shown that oxidizing fly ash samples using ozone that transforms the organic carbon into an oxide form dramatically reduces the AEA adsorption. Similarly, removing the organic carbon through heating the fly ash sample at 600°C also reduces the potential for AEA adsorption. Thus, measuring and quantifying the organic carbon is more advantageous when considering the air-entraining dosage of HVFAC. There are three distinct forms of organic carbon in fly ash: Volatile Organic Compounds (VOC), soot, and charcoal. Fan and Brown, (2001) quantified the VOC content by the color change after mixing fly ash with benzene and found that about 15 to 80% of unburnt carbon present in fly ash was VOC. Fan and Brown, (2001) hypothesized that VOCs in fly ash are aromatic carbons and come from volatilization of tar.

The second type of organic carbon is soot particles, which are generated because of partial combustion of hydrocarbons in a low oxygen environment. Soot particles are extremely small with an average size of 40 nm. The amount of soot particles in fly ash is difficult to measure using a conventional LOI test because oxidation of soot occurs slowly at 750°C and may not be effective at all. Soot particles can also adsorb AEA and decrease available air entrainment significantly if

present in large amounts (>10% of total carbon content). Gao et al., (1997) examined the presence of soot using high-resolution Transmission Electron Microscopy and found only trace amounts of soot in all their fly ash samples, which did not affect air-entrainment. To quantify soot particles in fly ash, Gao et al. (1997) recommended an “Optical Fine Particle Test” which involved dispersing fly ash in a colloidal 40 nm silica solution and then putting it in a centrifuge to remove all the larger particles of fly ash. Finally, absorbance at 500 nm is measured to obtain a qualitative measure of the amount of soot in the sample. This test is useful to confirm absence or significant presence of soot particles in fly ash.

The third type of organic carbon is charcoal or char. In general, the char particles are large enough to be seen by an optical microscope (Külaots et al., 2004). Most of the organic carbon in typical fly ash is in the form of charcoal. However, char does not contribute to AEA adsorption in proportion to its weight because of the relatively lower specific surface area compared to the other forms of carbon. Activated carbon used in low NO_x emission coal powerplants is also of charcoal type and is one exception because it has an extremely high specific surface area. Thus, activated carbon contaminated fly ash may have a very high AEA absorption capacity even if LOI is not high (Freeman et al., 1997).

Even though it is agreed that carbon present in fly ash affects air-entraining performance, there are only a few studies systematically investigating the types of carbon and their effect on air entrainment. The types of AEAs (ionic and non-ionic) chemically interact with the types of carbon in different manners because of the specific carbon’s specific surface area and surface charge density. The conventionally used LOI test only provides an approximate bulk carbon content but does not measure the soot particles or capture the effect of different types of carbons present in fly ash. A better understanding of soot, charcoal, and VOC contents in fly ashes sourced from different powerplants should provide more insight toward the effect of different coal-burning processes and coal sources on the fly ash quality and interaction with AEA.

4.2. Effect of Ca²⁺ and Mg²⁺ in Pore Solution

Replacement of cement with fly ash changes dissolution rates and thus affects the concentration of ions present in the solution. Anionic air-entraining agents are precipitated with increasing Ca²⁺ and Mg²⁺ concentrations (Baltrus and LaCount, 2001; Bruere, 1970; Jolicoeur et al., 2009). Divalent ion concentrations affect the AEA precipitation more than monovalent ions because of the higher charge density of the divalent ions (Somorjai and Li, 2010). The divalent cation concentration generally affects the performance of anionic air-entraining agents more than divalent anion concentration affects cationic air-entraining agents because the anions are larger in general, leading to a lower charge density.

B. Tests for Evaluating Air Entrainment. Many performance-based tests exist to quantify the air-entraining performance of concrete. As the properties of fly ash are important in the air-entraining of HVFAC, the relevant quality control tests are discussed in this section.

B.1. Concrete-Based Air Tests. The total air content and its distribution in a concrete mixture are the main ways to determine the performance of AEA. There are several standard methods to evaluate total air content in concrete in both the fresh and

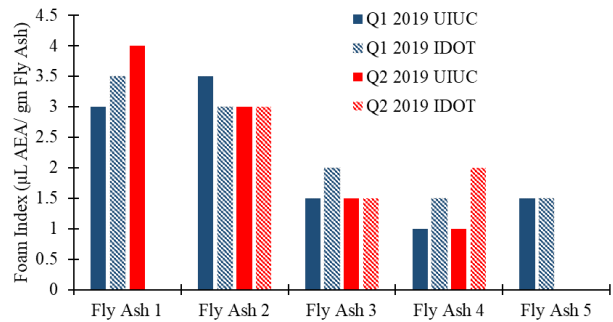


Fig. 6. Foam Index test results with Vinsol resin-based air-entraining admixture for five different fly ash sourced from powerplants in the Midwest at quarterly times (Q1, 2019 and Q2, 2019). Foam index tests run by authors (UIUC) and Illinois Department of Transportation (IDOT).

hardened state. Measuring bulk air content in fresh concrete can be done using three different methods: gravimetric (ASTM C138, 2017), pressure (ASTM C231, 2017) and volumetric (ASTM C173, 2016) with the pressure method the most common. Determination of the optimum AEA dosage to achieve the specified air content requires multiple mixtures for the standard mixing procedure. Ley, (2010) developed a more efficient method to determine the target air-entraining dosage from a single concrete mix by combining air content measurement through volumetric and pressure methods. In case of hardened concrete, ASTM C457, (2016) prescribes three standard test methods to evaluate the total air content and the air void distribution, i.e., linear-traverse method, modified point count method, and contrast-enhanced method. Recently, Ley et al. (2017) developed a test that can predict the freeze-thaw performance and air voids distribution of concrete by applying sequential pressure on fresh concrete, i.e., Super Air Meter, which is currently a provisional AASTHO TP 118 standard being used by multiple state DOTs.

B.2. Fly Ash-Based Foam Index Test. One common test method to understand the change of cementitious materials on the required AEA dosage is the Foam Index test. This test adds prescribed dosages of AEA to a diluted mix of water and cementitious materials until stable bubbles are formed. The stability of the bubble is assessed by the operator and thus, test variance is expectedly high. Figure 6 shows the variation in the foam index test for five fly ashes with two independent operators (UIUC and IDOT) and between two quarterly samples (Q1 and Q2) from the same power plant. The foam index test demonstrated that the required dosage would depend on the type of Illinois fly ash and could be as high as 3 µL AEA/gm fly ash. For different operators or the same operator but different quarterly sample in 2019, the foam index results were within ±1 µL AEA/gm fly ash.

As the foam index test is not a standard test, researchers have used different conditions to perform it since its introduction (Dodson, 1990). Harris et al., (2008a, 2008b, 2008c) studied the different test parameters, such as the container capacity versus amount of solution, mixing procedure, time of test, water to binder ratio, fly ash to binder ratio, etc. and proposed guidelines for a standardized test method given its known repeatability issues (Taylor et al., 2006b). Stencel et al., (2009) developed an automated foam index test that

measures the number of acoustic events and thus determines the foam stability, which can then be related to foam index. Recently, Watkins et al. (2015) proposed using a mechanical shaker to reduce the operator variability in the foam index test proposed by Harris et al., (2008a, 2008b, 2008c). Although the adsorption equilibrium between fly ash and AEA may take over an hour (Yu et al., 2000), the test duration was fixed to be 15 ± 3 minutes to make the test results more rapid. Even with these modifications, the foam index and LOI could not be correlated, especially at LOI less than 5% (Watkins et al., 2015). The foam index test still can provide for fly ash quality consistency but a standardized, simple, and rapid quality control test for fly ash is especially needed for evaluating air systems in HVFAC.

4. CONCLUSION

The application of high-volume fly ash concrete (HVFAC), defined as 40% fly ash replacement of cement by weight, to rigid pavements can improve initial cost, reduce the carbon footprint of concrete pavements, and decrease the heat of hydration during summer placements. Currently, the uncertainty in early age properties of HVFAC have limited its widespread application to pavements. The composition of fly ash and its chemical interaction with the cement and admixtures becomes more dominating in the overall hydration process, air system, and early age properties of HVFAC. This paper highlights additional tests needed to account for potential hydration reaction and air system changes with HVFAC.

Isothermal calorimetry provides data on heat evolved over time which can indicate setting times of the cement-fly ash combination and potential sulfate imbalance in an HVFAC mixtures. Calorimeter tests were run on two Illinois cement and four fly ash sources. The class C HVFAC mixes had a higher sulfate imbalance than class F mixes, with the initial set time delayed by 4.5 and 2 hours, respectively, compared to straight cement. Replacing 10% of the cement with nano limestone accelerated the initial and final setting time by 1.3 and 1.8 hours, respectively because of the nucleation effect of nano limestone. For HVFAC mixes, 10% nano limestone replacement accelerated the initial set time by 2.3 and 3.2 hours for class F and class C ashes, respectively. Existing literature mainly considers limestone as a filler material, although studies have shown its effect on changing the hydration of tricalcium aluminate by forming hydrated calcium monocarboaluminate. The effect of limestone on the chemistry of hydrated products in HVFAC is not well understood, and research efforts are needed in that direction for a better prediction of its early age properties.

Different types of carbon are present in fly ash, which affect the air-entraining performance of HVFAC with few studies collectively investigating the effect of volatile organic carbon, charcoal, and soot particles on air entrainment. The types of AEAs (ionic and non-ionic) will also adsorb on different types of carbon at varying rates, which is also not very well understood. Moreover, the concentration of divalent ions such as Ca^{2+} and Mg^{2+} also affect air entrainment as they can precipitate AEAs and thus reduce the amount of available AEAs for air bubble stabilization. Fundamental characterization of carbon and ions present in the pore solution is challenging to perform and thus, bulk quality control tests have been more popular. The foam index test has been used for 30 years as

a fly ash quality control test but is yet to be standardized because of the high variability in the results. For five fly ash sources in the Midwest, the foam index results indicated up to 3 μL AEA/gm fly ash difference in the required AEA dosage while for different operators performing the test on the same fly ash source, the foam index results were within ± 1 μL AEA/gm fly ash.

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