



# Application of internal curing for mixtures containing high volumes of fly ash

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## ABSTRACT

This paper focuses on testing performed on mixtures that would be consistent with the mortar portion of a concrete bridge deck mixture for many state departments of transportation. In this work a relatively large percentage of cement (40%, 60%, or 80% by volume) is replaced with Class C fly ash. To overcome concerns associated with slow set and early-age strength development that are often expressed with the high volume fly ash mixtures (HVFA), the water-to-cementitious materials ratio ( $w/cm$ ) by mass has been reduced from a conventional value of 0.42 to 0.30. To overcome potential complications that the low  $w/cm$  may cause in terms of self-desiccation, internal curing (IC) with prewetted lightweight aggregate was used to reduce shrinkage and increase hydration. By adopting this approach (lowering the  $w/c$  and using IC) IC HVFA mixtures show additional benefits that should permit their broader application.

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## 1. Background

Fly ash has historically been used in concrete transportation structures [1–5]. While one can consider fly ash as either an addition or as a cement replacement, it is truly the replacement of cement with fly ash that enables the fly ash to be considered as an efficient means to reduce the clinker content in the concrete. By reducing the clinker content per cubic yard, the  $CO_2$  generated in preparing the concrete can be reduced [6–10]. In addition, the use of fly ash has the potential benefits of reduced mixture cost, reduced embodied energy, and improved long-term concrete performance [11–16]. This is the reason why many producers and transportation agencies are aiming to use higher volumes of fly ash as a replacement for cement in their transportation structures. However, many hurdles exist to implementing this type of mixture. The hurdles include (1) potential incompatibilities among fly ash, admixtures, and cement; (2) strict limits on the maximum fly ash permitted and the time of the year that it can be used; (3) delays in set time [17] and strength development that slow construction operations; (4) concern about providing enough and proper curing; and (5) long-term durability concerning scaling and freeze/thaw issues [18,19]. For instance, a typical class C concrete bridge in the state of Indiana requires  $390 \text{ kg/m}^3$  of cementitious material, of which no more than 20% of cement by mass may be replaced by fly ash. Further, the Indiana Department of Transportation (INDOT)

specification limits fly ash to be used in the concrete mixture between April 1 and October 15 of the same calendar year [20].

The general approach used in this paper for developing High Volume Fly Ash (HVFA) concrete is using a lower water-to-cementitious materials ratio ( $w/cm$ ) to offset the expected slower strength development. This is also in agreement with recent tendencies of developing stronger and more durable concretes through the use of lower  $w/cm$ , corresponding to High Performance Concretes (HPCs). However, these beneficial properties also come with a drawback, as HPCs have been shown to be more sensitive to early-age cracking [21,22]. This early-age cracking may be due to increased temperature rise shortly after placement due to the high cement contents that are typically used, increased plastic shrinkage cracking due to reduced bleeding rates, and increased autogenous shrinkage [23]. While plastic shrinkage and thermal volume changes have been recognized in concrete construction over the last several decades and methodologies have been developed to deal with these effects, autogenous shrinkage is a problem that has gained attention more recently [24–27], because of the increased use of concrete in practice that contains water-reducing admixtures, enabling concretes to be made with lower  $w/cm$ .

Autogenous shrinkage is a deformation not caused by external influences (i.e., moisture transfer or temperature changes). Rather, autogenous shrinkage can be thought of as an ‘internal drying’ caused by the hydration reactions and their accompanying chemical shrinkage. Chemical shrinkage occurs when cement reacts with water as the reacted products occupy a smaller volume than the initial constituents [28,29]. In fluid systems (e.g., prior to set), this

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chemical shrinkage does not cause much concern and the entire system collapses on itself resulting in an externally measured volume change that is equal to the chemical shrinkage. However, after the concrete begins to harden, the structure of the cementitious matrix does not enable the externally measured volume change to be equal to the volume of chemical shrinkage [30]. As a result, vapor filled spaces are created within the matrix and stress begins to develop in the hardening paste [31]. This is commonly referred to as self-desiccation (i.e., internal drying). This ‘internal drying’ can be mitigated through the use of additional water during external curing. However, this technique has its limitations when low  $w/cm$  concretes are used, since depercolation of the capillary pores can happen at early ages, which limits movement of water to the core of the concrete. It has been proposed by several researchers [31–37] that an improved method for delivering ‘curing water’ to low  $w/cm$  concrete would be to place ‘packets or inclusions’ of water throughout the matrix rather than just placing the water at the surface. This is illustrated conceptually in Fig. 1.

## 2. Research approach

This study will evaluate a potential strategy for using high volumes of fly ash to replace cement. The work will seek to minimize potential reductions in early strength development that can occur with fly ash by using a lower  $w/cm$ . While a lower  $w/cm$  would be beneficial in terms of improved mechanical and transport properties, it has been shown that these mixtures may be more susceptible to early-age cracking. These mixtures will be internally cured to reduce self-desiccation which will reduce autogenous shrinkage and cracking potential while enabling more of the fly ash to react.

## 3. Proportioning mixtures for internal curing

Internal curing is achieved by using a prewetted fine light-weight aggregate (LWA) to provide the internal curing water. To proportion the internally cured mixtures a methodology is used that is based on a procedure developed by Bentz and Snyder [33], in which the amount of LWA is calculated based on the chemical shrinkage occurring in the sample. Eq. (1) permits the calculation of the amount of LWA based on this theory. It is interesting to note that fly ash will also contribute to the chemical shrinkage; therefore the equation must be based on the binder content, chemical shrinkage of the binder, and degree of reaction of the binder, respectively [38].

$$M_{LWA} = \frac{C_f \times CS \times \alpha_{max}}{S \times \phi_{LWA}} \quad (1)$$

where  $M_{LWA}$  (kg/m<sup>3</sup>) is the mass of LWA (in a dry state) that needs to be pre-wetted to provide water to fill in the voids created by chemical shrinkage,  $C_f$  (kg/m<sup>3</sup>) is the binder content of the mixture,  $CS$  (mL of water per g of binder) is the chemical shrinkage of the binder,  $\alpha_{max}$  (unitless) is the expected maximum degree of hydration (0 to 1),  $S$  (unitless) is the expected degree of saturation of the LWA and was taken to be 1 in this study when the dry LWA was soaked for 24 h, and  $\phi_{LWA}$  (kg of water/kg of dry LWA) is the absorption capacity of the LWA (taken here as the 24 h absorption value). It has been stated that it may be more appropriate to use desorption of the LWA down to some relative humidity (e.g., 94% RH) rather than its absorption [39]. Studies have described the measurement of this desorption and it is typically 90–95% of the 24 h absorption for many aggregates used in the United States, including the one used in this paper [40,41].

The use of HVFA concrete mixtures including IC may potentially be utilized to reduce shrinkage and shrinkage cracking [26]. Furthermore, the use of IC may provide a method to increase early-age strength gain and may enable the mixture to react for a longer time since water can be supplied to the concrete over a longer time period. For example, INDOT specifications recommend that fly ash mixtures be cured for longer durations. If we consider that IC can provide water over a longer period of time, it also provides a benefit in this sense.

## 4. Materials and mixture proportions

An ordinary Portland cement (OPC), ASTM C150-09 Type I/II, was used in this study, with a Blaine fineness of 476 m<sup>2</sup>/kg, a density of 3170 kg/m<sup>3</sup>, an estimated Bogue potential phase composition of 52% C<sub>3</sub>S, 18% C<sub>2</sub>S, 8% C<sub>3</sub>A, and 9% C<sub>4</sub>AF by mass, and a Na<sub>2</sub>O equivalent of 0.5% by mass. A Class C fly ash (ASTM C618-08a) was also used with a density of 2630 kg/m<sup>3</sup>. Chemical analyses of both cement and fly ash are summarized in Table 1. The particle size distributions (PSDs) of the cement and fly ash are shown in Fig. 2, each measured with laser diffraction.

The fine aggregate used was ordinary river sand with a fineness modulus of 2.71 and an apparent specific gravity of 2.58. Rotary kiln expanded shale (i.e., a lightweight fine aggregate) was used with a fineness modulus of 3.97 and a specific gravity (dry) of 1.38. The lightweight aggregate (LWA) was measured to have a 24 h water absorption of 17.5% by dry mass, when this material was tested using the paper towel technique [40,42]. A polycarboxylate-based high-range water-reducing admixture (HRWRA) was added at variable dosage by mass of cement in order to maintain the same (mini) slump of 13 mm (0.5 in.) in all mortars. The dimensions of the mini-slump cone are the following: top diameter of 19 mm (0.75 in.); bottom diameter of 38 mm (1.5 in.); and height of 57 mm (2.25 in.) [43]. These dimensions are in the same

Table 1

Chemical composition of the cement and fly ash used in this study.

Type/class	Cement fly I/II	Ash C
Silicon dioxide (SiO <sub>2</sub> ), %	19.97	38.71
Aluminum oxide (Al <sub>2</sub> O <sub>3</sub> ), %	4.81	19.15
Iron oxide (Fe <sub>2</sub> O <sub>3</sub> ), %	2.89	6.49
Calcium oxide (CaO), %	63.27	23.51
Magnesium oxide (MgO), %	1.54	5.29
Sulfur trioxide (SO <sub>3</sub> ), %	3.27	1.36
Potassium oxide (K <sub>2</sub> O), %	0.38	0.58
Sodium oxide (Na <sub>2</sub> O), %	0.28	1.64
Loss on ignition, %	2.88	0.30

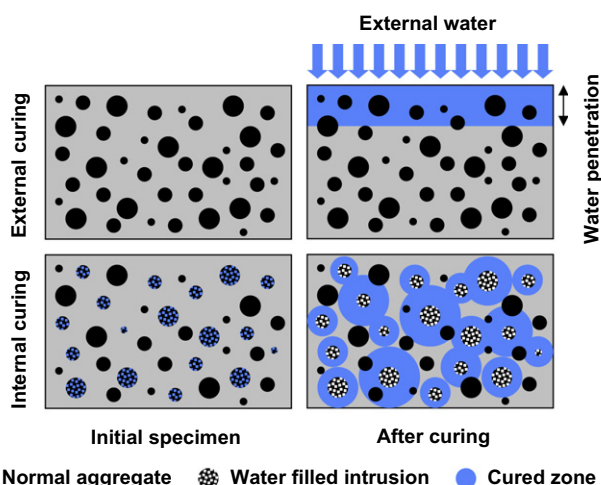
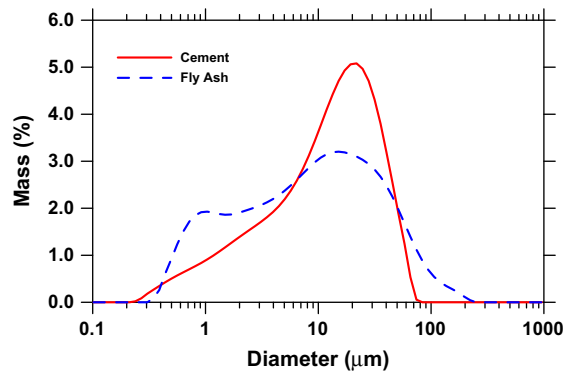


Fig. 1. Conceptual illustration of the differences between external and internal curing.



**Fig. 2.** Particle Size Distributions (PSDs) of cement and fly ash, as measured by laser diffraction.

proportions as the slump cone of ASTM C143. It is interesting to note that the amount of HRWRA was reduced as the fly ash content was increased (Table 2), likely due to the dilution in the cement content [17] and to the spherical shape of the fly ash particles compared to the angular shape of the cement particles. This effect may also provide a further decrease in the cost of these mixtures depending on the local availability of the materials.

A matrix of mortar mixtures was developed in which four  $w/cm$  levels and four fly ash replacement levels were evaluated. This matrix is shown in Table 2 (numbers in parentheses represent the HRWRA dosages by mass of binder for each mortar). Mortar with a  $w/cm$  of 0.42 and no fly ash represents a typical bridge deck concrete in the state of Indiana and is therefore taken as a reference. Not all the fly ash replacement levels were used in all mortars since fly ash enhances workability, and more prone-to-segregation specimens are thus obtained at higher  $w/cm$ . Fly ash replacement is made on a volume basis. While many current practices replace cement with fly ash on a mass basis, due to significant differences in their specific gravities this alters the total volume of paste in the concrete, having an effect on various concrete properties (e.g., strength, shrinkage, durability, workability). By using a volume replacement, the total paste volume in the concrete is maintained as constant and this is the reason why this approach was chosen.

In two of the fly ash mortars, corresponding to  $w/cm$  of 0.30 and fly ash contents of 40% and 60% by volume (bold values), a portion of the regular fine aggregate was replaced with prewetted LWA. It is important to note that the volume of aggregate (LWA and sand) remains constant at 55%, since only a portion of the sand was replaced with an equal volume of LWA. The replacement level for the LWA mixtures corresponds to the amount of LWA necessary to supply sufficient IC water to eliminate self-desiccation according to Eq. (1), with  $CS = 0.064$  mL water/g binder and  $\alpha_{max} = 0.83$ . The volume of mortar occupied by the LWA corresponds to 14.9% and 14.5% for the 40% and 60% fly ash mortars, respectively.

The mortars were prepared in accordance with ASTM C305-11. The LWA was oven dried, air cooled, and then submerged in water

for 24 h  $\pm$  1 h prior to mixing. The LWA was submerged in the total volume of water that included the mixing water needed for cement hydration and the water that would be absorbed by the LWA itself in 24 h. The excess water (water not absorbed into the LWA during 24 h) was then decanted and used as the mixing water for that particular mortar.

## 5. Experimental results

### 5.1. Mechanical properties

Three 102 mm diameter  $\times$  204 mm tall [4 in.  $\times$  8 in.] cylindrical specimens were prepared in accordance with ASTM C192/C192M-07 for each mortar mixture. At each age, three specimens were used to assess compressive strength (ASTM C39-10) and two specimens were used to measure the elastic modulus (ASTM C469-02) prior to strength testing. Following demolding at 1 d, all specimens were sealed in plastic bags and stored in an environmental chamber at 23  $^{\circ}\text{C} \pm 0.5$   $^{\circ}\text{C}$  [73.4  $^{\circ}\text{F} \pm 0.9$   $^{\circ}\text{F}$ ]. The cylinders were tested at several ages: (1, 3, 7, 14, 28, 91, and 365 d).

The results obtained can be observed in Fig. 3. As expected, as the  $w/cm$  is decreased, higher compressive strengths are achieved.

Under sealed conditions without IC and regardless of the  $w/cm$ , their self-desiccation will ultimately produce about the same volume fractions of empty porosity, although the empty pores will likely be larger in the higher  $w/cm$  mortar. While all of the cement in the  $w/cm$  of 0.42 sealed system should theoretically be able to hydrate, there would be a small fraction of unhydrated cement remaining in the sealed systems with  $w/cm$  of 0.36 and 0.30 due to water limitations (13% and 27%, respectively, according to Powers' Model [44]).

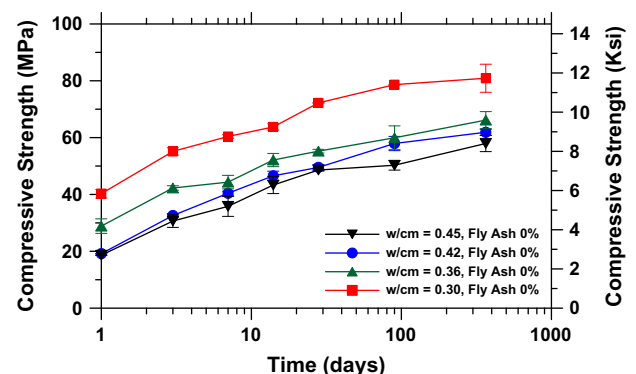
If fly ash is added without changing the  $w/cm$ , a slower strength development is typically observed. Fig. 4 shows the results. It is important to note that the reference mixture is the mortar with  $w/cm$  of 0.42. Mortar containing 40% fly ash has similar 1 d strength, and 60% fly ash mortar has similar 14 d strength, with strength increasing further at later ages in both cases. At 28 d, the concretes with 40% and 60% fly ash replacements have strengths that exceed that of the reference mixture by 52% and 17%, respectively, with similar improvements observed at 91 d and 365 d. Mortar containing 80% fly ash has equivalent strength at approximately 190 d; while it exceeds the strength of the reference mortar at 365 d by 11%.

IC through the use of prewetted LWA was also investigated using two of the mortars, and the results can be observed in Fig. 5. Under sealed curing conditions, IC enhances the 1 d strength by 13% and 61% in the 40% and 60% fly ash mortars, respectively. Both internally cured 40% and 60% fly ash mortars exceed the

**Table 2**

List of mortar mixtures prepared in the study. The proportions are shown primarily as a volumetric replacement; the mass replacement has also been added in square brackets parentheses along the top row (HRWRA dosages as mass percent of binder solids shown in parentheses).

$w/c$ or $w/cm$	Fly ash volume (%)				
	0 <sub>[0]</sub>	20 <sub>[17.2]</sub>	40 <sub>[35.7]</sub>	60 <sub>[55.5]</sub>	80 <sub>[76.9]</sub>
0.45	$X_{(0\%)}$	—	—	—	—
0.42	$X_{(0\%)}$	$X_{(0\%)}$	—	—	—
0.36	$X_{(0.3\%)}$	$X_{(0.1\%)}$	$X_{(0\%)}$	—	—
0.3	$X_{(0.5\%)}$	$X_{(0.35\%)}$	<b><math>X_{(0.2\%)}</math></b>	<b><math>X_{(0.1\%)}</math></b>	$X_{(0\%)}$



**Fig. 3.** Effect of decreasing  $w/cm$  on the compressive strength (Error bars represent the standard deviation from the average of three samples).

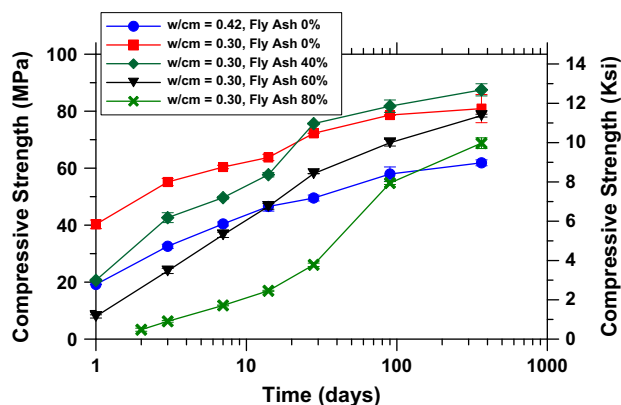


Fig. 4. Effect of adding high volumes of fly ash on the compressive strength (error bars represent the standard deviation from the average of three samples).

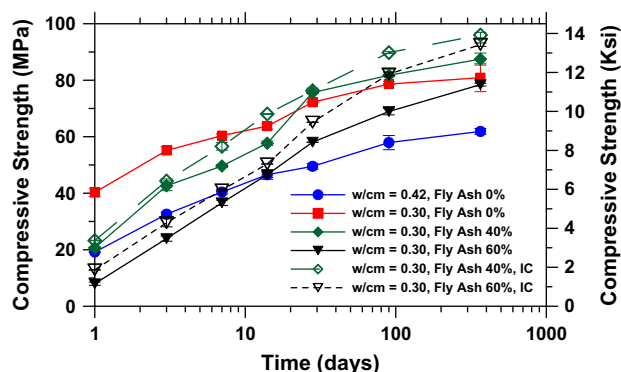


Fig. 5. Effect of including IC in HVFA mixtures on the compressive strength (error bars represent the standard deviation from the average of three samples).

reference strength ( $w/c$  of 0.42) by 54% and 32% at 28 d, and by 55% and 49% at 365 d, respectively. Isothermal calorimetry will be used later in this paper to indicate that these improvements in strength are most likely attributed to a higher degree of hydration reached in IC specimens. It should be noted that the HRWRA dosage was the same in the corresponding non-IC and IC mortars.

However, both IC and non-IC fly ash mortars are less stiff (i.e., lower modulus of elasticity) than the corresponding low  $w/c$  plain mortar (without fly ash) at early ages (Fig. 6). Considering this effect and the slower hydration occurring at early ages, more stress relaxation in restrained conditions should be expected. These property differences should produce a reduction in early-age cracking [45,46].

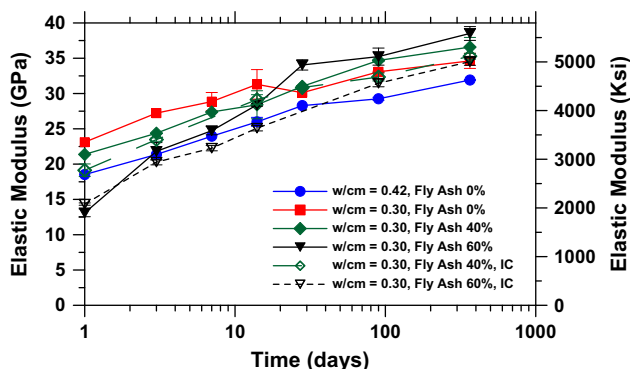


Fig. 6. Effect of including IC in HVFA mixtures on the elastic modulus (error bars represent the standard deviation from the average of two samples).

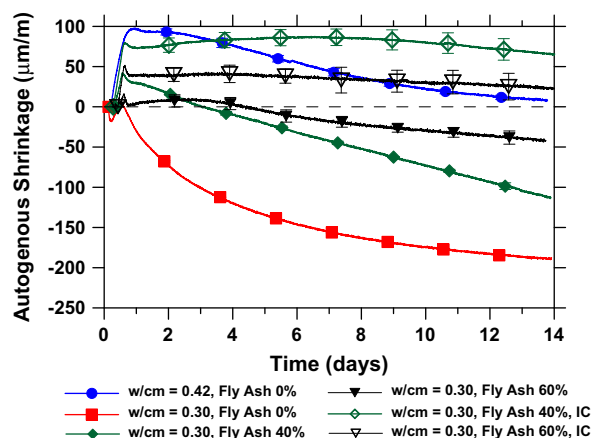


Fig. 7. Autogenous shrinkage as a function of time (error bars represent the standard deviation from the average of three samples).

## 5.2. Shrinkage performance

As previously mentioned, a major concern when low  $w/cm$  mixtures are used is autogenous deformation and cracking that can occur at early ages. Linear autogenous shrinkage measurements were performed according to ASTM C1698-09. Each mortar was encapsulated in thin, corrugated polyethylene molds, with a length-diameter ratio of approximately 420 mm:25 mm [16.5 in.:1 in.]. The mortar was cast into the molds and vibrated. The specimens were then sealed at the ends to prevent moisture loss and placed over supports provided with spring loaded LVDT's at each end to continuously record the displacement into a data logger every 5 min during two weeks while maintained at a temperature of  $23 \pm 0.5^\circ\text{C}$  [ $73.4^\circ\text{F} \pm 0.9^\circ\text{F}$ ]. Fig. 7 shows the measured autogenous shrinkage in six mortar mixtures.

As expected, lower total autogenous shrinkage is initially observed in HVFA mortars compared with the non-fly ash mortar with  $w/cm$  of 0.30, which is explained by the fact that fly ash samples contain a lower amount of cement, so that the initial reaction rate and water consumption is lower. However, at later ages, the rate of shrinkage is higher in fly ash mortars (i.e., the slope of the autogenous shrinkage response). This is important to note as this can lead to more shrinkage than a conventional concrete (e.g., between 1 week and a month) which can make this concrete more susceptible to cracking. IC further reduces autogenous shrinkage in fly ash samples, keeping them above 'zero' net shrinkage at 14 d, indicating that the samples exhibited a slight net expansion during this period of time.

The difference in shrinkage behavior can also be explained by the size of the pores that are being emptied during hydration. The size of the emptied pores is related to the internal relative humidity (RH) measured in the samples. Lower RH's indicate smaller pore sizes being emptied and higher autogenous deformations, since more "self-desiccation" (i.e. internal drying) is occurring in the samples.

RH was measured using Rotronic HygrClip2S<sup>1</sup> sensors ( $\pm 0.8\%$  RH at  $23 \pm 0.1^\circ\text{C}$  [ $73.4^\circ\text{F} \pm 0.2^\circ\text{F}$ ]). Probes were mounted in a 75 mm  $\times$  68 mm [2.95 in.  $\times$  2.7 in.] stainless steel cylinder that was placed over a water jacketed sample cup holder. The water jacket was connected with a programmable water bath; however, for

<sup>1</sup> Certain commercial products are identified in this paper to specify the materials used and procedures employed. In no case does such identification imply endorsement or recommendation by the National Institute of Standards and Technology, Purdue University or Catholic University of Chile, nor does it indicate that the products are necessarily the best available for the purpose.



this study the samples were maintained at a constant temperature ( $23.0\text{ }^{\circ}\text{C} \pm 0.1\text{ }^{\circ}\text{C}$  [ $73.4\text{ }^{\circ}\text{F} \pm 0.2\text{ }^{\circ}\text{F}$ ]). The 10 g samples were placed in 12 mm [0.47 in.] deep cups with a 43 mm [1.7 in.] diameter. The sensor was compared with reference salts (potassium sulfate, potassium chloride, and sodium chloride) to provide a point of calibration. Data were recorded at 5 min intervals. Fig. 8 shows typical relative humidity measurements over the mortars used in this study. The lower  $w/cm$  mixtures have smaller size pores emptied by self-desiccation and as such they produce a lower internal RH. It is interesting to note that as fly ash replacement level is increased, RH also increases. This is due in part to the water demand, as there is less cement reacting and partially due to the pore size distribution. IC supplies water from the much larger pores within the LWA to fill in the water being lost from the pores so that the smaller pores remain filled and the relative humidity is higher. Therefore, a reduction in shrinkage deformations is expected, occurring at the same time that the stresses develop in restrained samples.

As mentioned above, fly ash starts reacting at later times and consequently less autogenous shrinkage is observed at early ages. Chemical shrinkage (CS) was measured during the first 7 d of reaction to estimate the rate of reaction and to better understand the values for CS that should be used in Eq. (1). Three of the mortar samples were used for assessing the chemical shrinkage according to a modified version of the ASTM C1608-07 in which the height of the water in the capillary tube was recorded continuously using a pressure sensor [47]. Fig. 9 shows that there is less chemical shrinkage at early ages in the samples containing fly ash when the chemical shrinkage is normalized by the mass of binder; however this will be a greater value if normalized by the mass of cement. This is important and shows why Eq. (1) should be modified to be designed based on binder and not only Portland cement.

Mortar rings were prepared in accordance with ASTM C1581-04, using steel rings instrumented with four strain gages each. Three mortar specimens were prepared for each mixture. A data acquisition system was set up so that shrinkage deformation data was collected every 5 min from 30 min after casting the specimens. They were kept in their molds for 24 h in an environmental chamber at  $23\text{ }^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$  [ $73.4\text{ }^{\circ}\text{F} \pm 0.9\text{ }^{\circ}\text{F}$ ]. After 24 h, the specimens were demolded, sealed with aluminum foil to minimize evaporation, and placed again back in the environmental chamber. By doing this, the effect of internal curing water in the sample could be better observed. Further shrinkage measurements were taken up to 28 d.

Again, a lower shrinkage rate is observed in HVFA mortars at early ages, if compared to a plain mortar with  $w/c$  of 0.30 and no fly ash. This is translated into lower stresses developed in the samples during the first days of curing (Fig. 10). However, as chemical reaction and chemical shrinkage develop more slowly and to a higher extent, specimens with fly ash are more likely to crack at

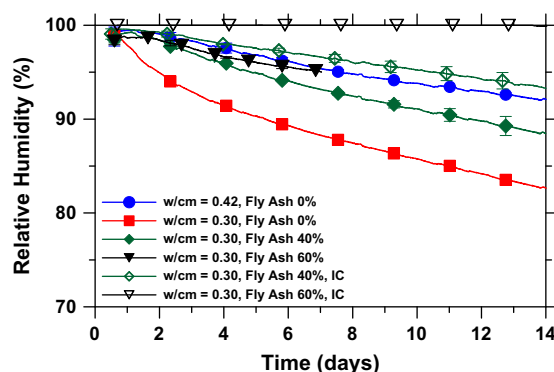


Fig. 8. Measured internal relative humidity of an aging mortar (error bars represent the standard deviation from the average of two samples).

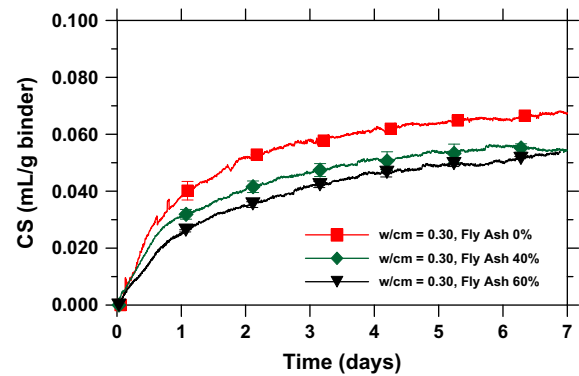


Fig. 9. Chemical shrinkage in mortar samples (error bars represent plus and minus one standard deviation from the average of two samples).

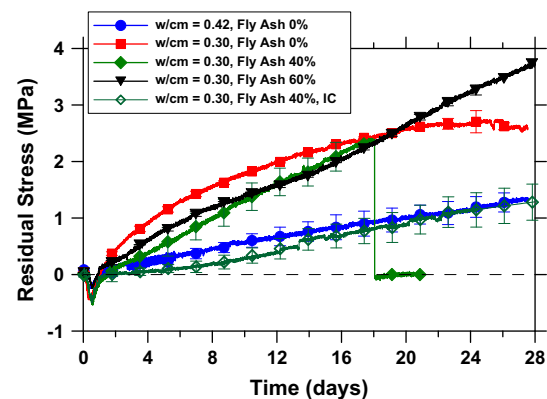


Fig. 10. Stress developed in ring specimens as a function of time (error bars represent the deviation from the average of two samples).

later ages. For example, in this study, the  $w/cm = 0.30$ , 40% fly ash mortar without IC cracked after 18 d, while the  $w/cm = 0.30$  no fly ash mortar did not crack during the 28 d evaluation period. The 40% fly ash IC mortar exhibited a stress development quite similar to that of the original  $w/cm = 0.42$  mortar without fly ash throughout the 28 d measurement.

### 5.3. Semi-adiabatic temperature rise

Early-age cracking due to the thermal effects can be common in high performance concrete due to its low  $w/cm$  and high paste volume. To demonstrate another potential benefit of using higher volumes of fly ash in concrete, a simple test, similar to semi-adiabatic calorimeter, was employed. This test consisted of placing a mortar cylinder ( $15.25\text{ cm} \times 17.8\text{ cm}$  [6 in.  $\times$  7 in.]) inside an insulated chamber made from a high refractory ceramic insulation material (Zircar Microsil<sup>1</sup>), creating a quasi(semi)-adiabatic chamber with a very low thermal coefficient. The temperature history of the mortars was measured over 4 d in the insulated chamber as shown in Fig. 11.

The maximum heat developed by the 40% fly ash mortar produces a temperature that is approximately the same as the plain mortar with a  $w/cm$  of 0.42 (being only 3.4% higher). A lower temperature rise was observed in the 60% fly ash mortar (20% lower compared to the reference mortar). While these observations have been made by others using supplementary cementitious materials, this shows a clear indication that the lower  $w/cm$  does not result in substantially greater heat rise when fly ash is used. IC does not appreciably change the temperature profile for either the 40% or the 60% fly ash mortars.

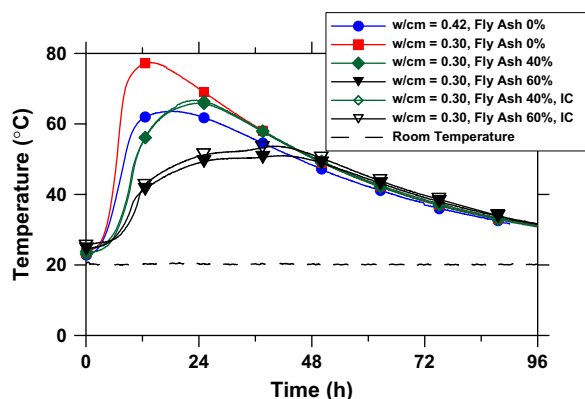


Fig. 11. Temperature rise as a function of time.

#### 5.4. Influence of fly ash on the hydration rate and strength development

HVFA mixtures are often characterized by their slower rate of early-age reaction and strength development. This can be examined using isothermal calorimetry. Approximately 15 g of an externally mixed mortar were weighed and placed in a glass ampoule, which was then capped and placed into the isothermal calorimeter about 10 min after cement was mixed with water. Fig. 12 shows the results obtained in the mortars being studied in this research over the course of 14 d.

The results were normalized by mL of initial water (i.e., initial porosity). By doing this, and assuming that the volume of created hydration products is proportional to the heat generated, one can potentially relate the space-filling capabilities of the hydration products with strength [48]. A slower heat development is observed with increasing fly ash replacement level as the fly ash is less reactive than the cement, though the fly ash can provide additional space between the cement particles and can act as a nucleating agent which both increase the hydration rate of the cement. After 14 d, the rate of heat evolved in the 40% fly ash IC mixture is higher than that in the plain mortars, indicating more reaction taking place in the fly ash systems. This increased rate of reaction can help explain the increased autogenous shrinkage rate, increased chemical shrinkage rate, and increased strength at intermediate ages.

It is interesting that if one plots the cumulative heat release versus strength development (Fig. 13), all of the mixtures prepared in this study follow a single line ( $R^2 = 0.972$ ). This correlation between early age cumulative heat release and strength has been observed in other systems as well [49–51]. Fig. 13 can be a powerful tool for using isothermal calorimetry to estimate strength at early ages in these mortar mixtures.

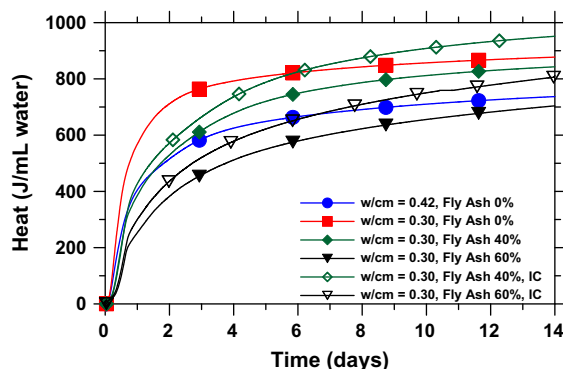


Fig. 12. Cumulative heat released (Isothermal) curves vs. time on a per milliliter of water basis.

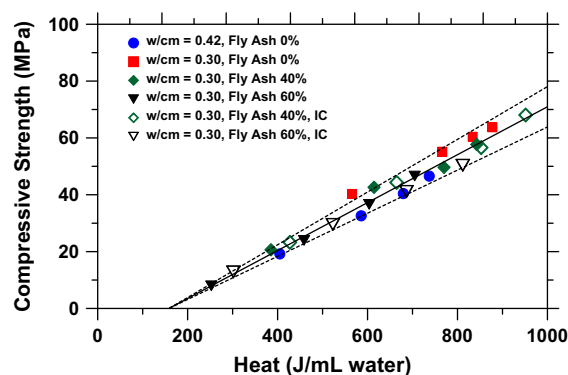


Fig. 13. Measured compressive strengths vs. measured cumulative heat on a per milliliter initial water basis for mortars at the ages of 1, 3, 7, and 14 d. Solid line shows the best fit while the two dashed lines indicate  $\pm 10\%$  from the best fit.

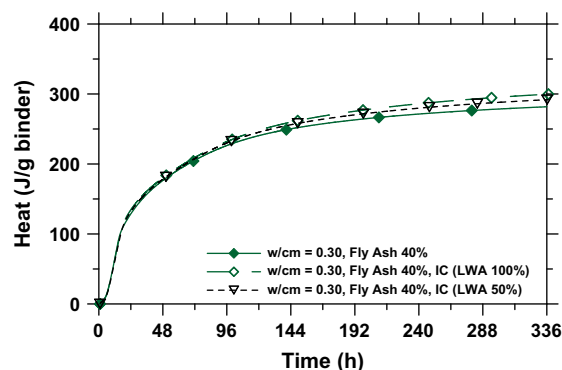


Fig. 14. Effect of changing IC replacement level.

The use of IC results in a slight increase in the heat developed at early ages (24 h) due to increased cement reaction [52–54] however it does not appreciably alter the rate of reaction as shown in Fig. 14. Though not used in this work, powder additions such as rapid set cement, calcium hydroxide, fine limestone, or aluminates or the addition of a conventional chemical admixture (e.g., non-chloride accelerator) could be strategies to mitigate these early-age deficiencies, if they exist, (retardation and the accompanying set time delays) in HVFA mixtures [51,55,56].

## 6. Conclusions

A matrix of several HVFA mortars was prepared for use in this study. The mixtures all had a similar fresh workability performance as defined in terms of slump. Numerous tests were performed to evaluate the properties of these mortars including: compressive strength, modulus of elasticity, free and restrained shrinkage, measurement of internal relative humidity, isothermal calorimetry, and semi-adiabatic temperature rise. The  $w/cm$  was reduced to compensate for slow strength development with high volumes of fly ash. Internal curing was used to counteract the drawbacks of using low  $w/cm$  concretes in terms of shrinkage cracking, while providing additional water to support the fly ash reactions. Several conclusions can be drawn from this study:

- (1) HVFA mixtures with  $w/cm$  of 0.30 have higher strength at later ages (28 d, 91 d, and 365 d) compared to the reference mortar. In particular, the 40% fly ash mortar had an equivalent 1 d strength if compared to a mortar with  $w/cm$  of 0.42 (reference mixture in this study), whereas the 60% fly ash mortar had equivalent strength at 14 d.

- (2) IC enhances the 1 d strength by 13% and 61% in the 40% and 60% fly ash mortars, cured under sealed conditions, respectively. The effect of IC at later ages is more evident; it results in a higher strength achieved if compared to the reference  $w/c = 0.42$  mortar (55% and 49% higher at 365 d in internally cured 40% and 60% fly ash mortars, respectively).
- (3) A lower modulus of elasticity is obtained when either fly ash, IC, or a combination of both are included in the mixture. IC addition reduces the elastic modulus by an average of 7% and 11% in 40% and 60% fly ash mortars, respectively.
- (4) The slower hydration reaction in the fly ash mixtures results in less initial autogenous shrinkage deformations at early ages. However, the rate of autogenous shrinkage remains high in the fly ash mixtures at later ages. This increases their potential for cracking at later ages. The use of IC can be a beneficial method to reduce stress development caused by restrained shrinkage. The reduction in shrinkage observed is mainly due to a higher internal RH maintained in these systems.
- (5) IC does not significantly offset the retardation or slow strength observed when high fly ash volumes are used. Other means to accelerate the hydration process may be available [51,55,56].
- (6) Lowering the  $w/cm$  increases the potential of heat generation and thermal cracking; however the addition of high volumes of fly ash has shown benefits in this regard.
- (7) Although IC does not alter the initial rate of the hydration reaction during the first hours (where other means of mitigating the retardation effect observed in HVFA mixtures should be used), the importance of properly calculating the amount of LWA needed in internally-cured concrete mixtures is exemplified in Fig. 14, where different amounts of LWA were used producing a difference in the degree of hydration achieved in each system at later ages (i.e. 7 d).

A detailed economic analysis was not performed, since economics are strongly influenced by local costs and availability of materials. However, replacement of cement with fly ash should produce a cost reduction that, in the vast majority of cases, will outweigh the increased cost of using LWA. When a life cycle analysis is considered and/or if carbon trading is considered, the HVFA mixtures should have even more benefits.

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## References

- [1] Davis RE, Carlson RW, Kelly JW, Davis AG. Properties of cements and concretes containing fly ash. *Proc, Am Concr Ins* 1937;33:577–612.
- [2] Halstead WJ. Use of fly ash in concrete. NCHRP 127 (October). Washington: Transportation Research Board, National Research Council; 1986.
- [3] Helmuth R. Fly ash in cement and concrete. Skokie, Ill: Portland Cement Association; 1987.
- [4] Malhotra VM, Ramezaniapour A. Fly ash in concrete. 2nd ed., CANMET. Energy, mines and resources Canada, Ottawa; 1994. p. 307.
- [5] ACI-232, Use of fly ash in concrete. ACI 232.2R. ACI Committee report; 1996. p. 34.
- [6] Malhotra VM. Role of supplementary cementing materials in reducing greenhouse gas emissions CANMET. In: Gjorv Odd, Sakai Koji, editors. Concrete technology for a sustainable development in the 21st century. Spon Press; 1999. p. 400.
- [7] Malhotra VM. Making concrete “Greener” with fly ash. *ACI Concr Int* 1999;21(5):61–6.
- [8] Worrell E, Price L, Martin N, Hendriks C, Ozawa L. Carbon dioxide emissions from the global cement industry. *Ann Rev Energy Environ* 2001;26:303–29.
- [9] Mehta PK. Greening of the concrete industry for sustainable development. *ACI Concr Int* 2002;24(7):23–8.
- [10] McCaffrey R. Climate change and the cement industry. *Global Cem Lime Mag* 2002(Environmental Special Issue):15–9.
- [11] Malhotra VM. Durability of concrete incorporating high-volume of low calcium (ASTM Class F) fly ash. *Cem Concr Compos* 1990;12(4):271–7.
- [12] Hansen T. Long term strength of fly ash concretes. *Cem Concr Res* 1990;20(2):193–6.
- [13] Thomas MDA, Matthews JD. Carbonation of fly ash concrete. *Mag Concr Res* 1992;44(160):217–28.
- [14] Bilodeau A, Sivasundaram V, Painter K, Malhotra VM. Durability of concrete incorporating high volumes of fly ash from sources in the USA. *ACI Mater J* 1994;91(1):3–12.
- [15] Naik T, Singh S, Ramme B. Mechanical properties and durability of concrete made with blended fly ash. *ACI Mater J* 1998;95(4):454–62.
- [16] Ramlochan T, Zacarias P, Thomas MDA, Hooton RD. The effect of pozzolans and slag on the expansion of mortars cured at elevated temperature, PART I: expansive behaviour. *Cem Concr Res* 2003;33(6):807–14.
- [17] Bentz DP, Ferraris C. Rheology and setting of high volume fly ash mixtures. *Cem Concr Compos* 2010;32(4):265–70.
- [18] Neuwald A, Krishnan A, Weiss WJ, Olek J, Nantung TE. Curing and its relationship to measured scaling in concrete containing fly ash. In: Transportation research board 2003, annual meeting CD-ROM; 2003.
- [19] Krishnan A, Metha JK, Olek J, Weiss WJ. Technical issues related to the use of fly ash and slag during late-fall (low temperature) construction season. Publication FHWA/IN/JTRP-2005/05. In: Joint transportation research program. West Lafayette, Indiana: Indiana Department of Transportation and Purdue University; 2006. <<http://dx.doi.org/10.5703/1288284313382>>.
- [20] INDOT, Indiana Department of Transportation Specifications for Contractors. Section 500 – Concrete Pavements, 2011 Standard Specification Book. <<http://www.in.gov/dot/div/contracts/standards/book/sep11/5-2012.pdf>>
- [21] Weiss WJ, Yang W, Shah SP. Factors influencing durability and early-age cracking in high strength concrete structures, SP 189-22 high performance concrete: research to practice, Farmington Hills, MI, 1999; 387–409.
- [22] Shah SP, Weiss WJ. High performance concrete: strength, permeability, and shrinkage cracking. In: Proceedings of the PCI/FHWA international symposium on high performance concrete 2000, Orlando, FL; 2000. p. 331–40.
- [23] Shah S, Weiss J, Yang W. Shrinkage cracking in high performance concrete. In: Proceedings of the PCI/FHWA international symposium on high performance concrete, New Orleans, LA; 1997.
- [24] Shah SP, Weiss WJ, Yang W. Shrinkage cracking-can it be prevented? *Concr Int* 1998;20(4):51–5.
- [25] RILEM early age cracking in cementitious systems. Bentur A, editor. Report of RILEM technical committee 181-EAS; 2003. p. 350.
- [26] Brown M, Smith C, Sellers G, Folliard K, Breen J. Use of alternative materials to reduce shrinkage cracking in bridge decks. *ACI Mater J* 2007;104(6):629–37.
- [27] Bentz DP, Peltz MA. Reducing thermal and autogenous shrinkage contributions to early-age cracking. *ACI Mater J* 2008;105(4):414–20.
- [28] Le Chatelier H. Sur les Changements de Volume qui Accompagnent le durcissement des Ciments, Bulletin Societe de l'Encouragement pour l'Industrie Nationale, Seme serie, tome 5, Paris; 1900.
- [29] L'Hermite RG. Volume changes of concrete. In: 4th International symposium on the chemistry of cement. Washington, DC; 1960.
- [30] Sant G, Lura P, Weiss J. Measurement of volume change in cementitious materials at early ages: review of testing protocols and interpretation of results. *Transport Res Rec* 2006;1979:21–9.
- [31] Jensen OM, Hansen PF. Water-entrained cement-based materials: I. Principles and theoretical background. *Cem Concr Res* 2001;31(4):647–54.
- [32] Philleo R. Concrete science and reality. In: Skalny JP, Mindess S, editors. Materials science of concrete II American ceramic society. Westerville, OH; 1991.
- [33] Bentz DP, Snyder KA. Protected paste volume in concrete: extension to internal curing using saturated lightweight fine aggregate. *Cem Concr Res* 1999;29(11):1863–7.
- [34] Bentz DP, Jensen OM. Mitigation strategies for autogenous shrinkage cracking. *Cem Concr Compos* 2006;26(6):677–85.
- [35] RILEM, Report 41: internal curing of concrete. Kovler K, Jensen OM, editors. Internal Curing of Concrete. RILEM Publications S.A.R.L.; 2007.
- [36] Henskensiefken R, Castro J, Bentz DP, Nantung TE, Weiss J. Water absorption in internally cured mortar made with water-filled lightweight aggregate. *Cem Concr Res* 2009;39(10):883–92.
- [37] ACI. Report on early-age cracking: causes, measurement and mitigation (ACI 231R-10). American Concrete Institute – Committee 231, Farmington Hills, MI; 2010. 48p.

- [38] Bentz DP, Weiss J. Internal curing: a 2010 state of the art review. National NISTIR 7765. Institute of Standards and Technology, US Department of Commerce, Gaithersburg, MD; 2011.
- [39] Bentz DP, Lura P, Roberts JW. Mixture proportioning for internal curing. *Concr Int* 2005;27(2):35–40.
- [40] Castro J, Keiser L, Golias M, Weiss J. Absorption and desorption properties of fine lightweight aggregate for application to internally cured concrete mixtures. *Cem Concr Compos* 2011;33:1001–8.
- [41] Pour-Ghaz M, Castro J, Klavivko EJ, Weiss J. Characterizing lightweight aggregate desorption at high relative humidities using a pressure plate apparatus. *J Mater Civil Eng* 2011. <[http://dx.doi.org/10.1061/\(ASCE\)MT.1943-5533.0000422](http://dx.doi.org/10.1061/(ASCE)MT.1943-5533.0000422)>.
- [42] NYDOT. Test Method No.: NY 703-19 E. Moisture content of lightweight fine aggregate. New York State Department of Transportation, Materials Bureau, Albany, NY; August 2008.
- [43] Kantro DL. Influence of water-reducing admixtures on properties of cement paste—a miniature slump test. *Cem, Concr, Aggre* 1980;2:95–102.
- [44] Powers TC. A discussion of cement hydration in relation to the curing of concrete, vol 25. Bulletin: Portland Cement Association; 1948. p. 188.
- [45] Shin KJ, Bucher BE, Weiss J. The role of low stiffness aggregate particles on the restrained shrinkage cracking behavior of mortar. *J Civil Eng Mat* 2011;23(5):597–605.
- [46] Shin KJ, Castro J, Schlitter J, Golias M, Pour-Ghaz M, Henkensiefken R, et al. Handbook of concrete durability. In: Kim S-H, Ann KY, editors. The role of internal curing as a method to improve durability. Middleton Publishing Inc.; 2010.
- [47] Peethamparan S, Weissinger E, Vocaturo J, Zhang J, Scherer G. Monitoring chemical shrinkage and hydration kinetics using pressure sensors. ACI special proceedings in CD on advances in the material science of concrete, SP-270. 2010, p. 77–88.
- [48] Bentz DP, Barrett T, De la Varga I, Weiss J. Relating compressive strength to heat release in mortars. *Adv Civ Eng Mater* 2012, accepted for publication.
- [49] Bentz DP. Blending different fineness cements to engineer the properties of cement-based materials. *Mag Concr Res* 2010;62(5):327–38.
- [50] Bentz DP, Durán-Herrera A, Galvez-Moreno D. Comparison of ASTM C311 strength activity index testing vs. testing based on constant volumetric proportions. *J ASTM Int* 2012;9(1):7.
- [51] Bentz DP, Sato T, De la Varga I, Weiss J. Fine limestone additions to regulate setting in high volume fly ash mixtures. *Cem Concr Compos* 2012;34(1):11–7.
- [52] Lura P, Winnefeld F, Klemm S. Simultaneous measurements of heat of hydration and chemical shrinkage on hardening cement pastes. *J Therm Anal Calorim* 2010;101(3):925–32.
- [53] Geiker M. Studies of Portland cement hydration by measuring of chemical shrinkage and a systematic evaluation of hydration curves by means of the dispersion model. PhD Dissertation, 1983. Technical University of Denmark; 1983.
- [54] Castro J, De la Varga I, Weiss J. Using isothermal calorimetry to assess water absorption of fine LWA in mortars. *J Mater Civil Eng*, submitted for publication. <[http://dx.doi.org/10.1061/\(ASCE\)MT.1943-5533.0000496](http://dx.doi.org/10.1061/(ASCE)MT.1943-5533.0000496)>.
- [55] Bentz DP. Powder additions to mitigate retardation in high volume fly ash mixtures. *ACI Mater J* 2010;107(5):508–14.
- [56] Gurney L, Bentz DP, Sato T, Weiss J. Using limestone to reduce set retardation in high volume fly ash mixtures: improving constructability for sustainability. Transportation Research Record, Construction Materials, 2012.