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Optimization of cement and fly ash particle sizes to produce sustainable concretes

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ABSTRACT

In the drive to produce more sustainable concretes, considerable emphasis has been placed on replacing cement in concrete mixtures with more sustainable materials, both from a raw materials cost and a CO_2 footprint perspective. High volume fly ash concretes have been proposed as one potential approach for achieving substantial reductions in cement usage, but their usage is sometimes hampered by reduced early age strengths and dramatically increased setting times. One limitation of the current industry practice is that portland cements are generally only optimized for their performance in a pure cement, as opposed to a blended cement, system. In this paper, a new approach of optimizing the particle sizes of the cement and fly ash for achieving desired performance in a blended product will be presented. By appropriately selecting the particle size distributions of cement and fly ash, equivalent 1 d and 28 d strengths may be achieved with about a 35% volumetric replacement of cement with fly ash, while maintaining the same volume fraction of water in the mixture, thus providing an actual 35% reduction in cement content.

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1. Introduction

It has been reported that the particle size distribution (PSD) of cement plays a major role in influencing the fresh and hardened properties of cement-based materials, particularly at early ages [1–9]. In fact, one of the major trends in concrete technology in the past 50 years has been an increase in the fineness of cement [10], mainly to provide increased early-age strengths to support fast track construction. These cements, however, are essentially optimized for utilization as the sole binder in concrete, without regard to potential blended cement concretes. Another more recent trend, partially in response to an increased focus on sustainability, is an increase in the utilization of supplementary cementitious materials (SCMs), such as slag, fly ash, and silica fume in concretes. One example of this trend would be the movement towards high volume fly ash (HVFA) concretes, where 50% or more of the cement is replaced with fly ash [11–13]. Replacing a portion of the cement with an SCM often reduces early-age strengths and produces delayed setting times, for mixtures formulated at the same water-to-cementitious materials ratio (*w/cm*) [14]. For these reasons, in the current industry practice, a reduction in *w/cm* is typically implemented in HVFA mixtures, to increase their early-age strengths and decrease their setting times, respectively. In addition or alternatively to lowering *w/cm*, early-age strength in HVFA mixtures is sometimes increased by increasing the volume fraction of the cementitious binder in a concrete.

When the *w/cm* of an HVFA mixture is reduced relative to that of an ordinary portland cement concrete of equivalent performance, care must be exercised when translating the replacement level value for a concrete mixture into its equivalent cement content reduction, as the two are usually not identical. As an example, a concrete with a *w/cm* of 0.30 by mass, with a 40% volumetric replacement of fly ash for cement, actually may only achieve about a 25% reduction in cement content relative to an equivalently performing concrete mixture based solely on portland cement with a water-to-cement ratio (*w/c*) of 0.42. In addition to reducing the true cement savings achieved in an HVFA mixture, this practice often requires an increase in the dosages of costly chemical admixtures, usually including a high range water reducing admixture (HRWRA) and perhaps an accelerator to further offset the delayed setting times and low early-age strengths that are often prevalent in an HVFA mixture. While current techniques for engineering concrete to use SCMs are well-established and usually produce good results, there are still some concrete manufacturers that choose not to use SCMs or use them only in small quantities.

Cements that have been optimized with respect to fineness and sulfate content for a 100% cement binder concrete may not be optimal for utilization in a blended cement HVFA product. With this limitation in mind, Roman Cement LLC has recently been awarded a patent for "High Early Strength Pozzolan Cement Blends," where the PSDs of the cement and the pozzolan are controlled to produce "optimum" (early age) properties [15]. As indicated above, delayed

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Table 1
Experimental design employed in the present study.

Mixture order (3–18)	Encoded variable levels			Original (targeted) variables			HRWRA dosage (g/100 g binder)
	A = cement PSD	*B* = fly ash PSD	*C* = FA content = (*A* + *B*) mod 4	D_{90} cement (μm) [ID #]	D_{10} fly ash (μm) [ID #]	Volumetric fly ash content (%)	
9	0	0	0	7.5 [10]	5 [5]	20	1.00
10	0	1	1	7.5 [10]	10 [4]	35	0.67
12	0	2	2	7.5 [10]	15 [3]	50	0.05
7	0	3	3	7.5 [10]	20 [2]	65	0.00
8	1	0	1	10 [9]	5 [5]	35	0.48
6	1	1	2	10 [9]	10 [4]	50	0.28
18	1	2	3	10 [9]	15 [3]	65	0.00
17	1	3	0	10 [9]	20 [2]	20	1.00
16	2	0	2	15 [8]	5 [5]	50	0.05
11	2	1	3	15 [8]	10 [4]	65	0.00
14	2	2	0	15 [8]	15 [3]	20	0.80
5	2	3	1	15 [8]	20 [2]	35	0.37
15	3	0	3	20 [7]	5 [5]	65	0.00
13	3	1	0	20 [7]	10 [4]	20	0.05
3	3	2	1	20 [7]	15 [3]	35	0.00
4	3	3	2	20 [7]	20 [2]	50	0.00

setting times and low early age strengths are two of the most common problems associated with the production of HVFA concretes [11–14]. The basic premise of the patented approach is that blending a finer cement with a coarser fly ash may produce a superior product, in terms of increasing early age strengths while maintaining later age performance. This paper presents the results of using design of experiment principles to demonstrate the viability of this approach in a set of mortar specimens with constant volume fractions of water and sand. Full details of the complete study can be found in a recently issued NIST report [16].

2. Experimental program

A commercially available Type I/II (ASTM C150 [17]) cement and a Class F fly ash (ASTM C618 [18]) were obtained from a manufacturer and a supplier, respectively. According to its manufacturer, the cement has a Blaine fineness of 376 m^2/kg and a potential Bogue phase composition of 57% C_3S, 15% C_2S, 7% C_3A, and 10% C_4AF by mass. Its measured density is 3200 kg/m^3 ± 10 kg/m^3 (ASTM C188 [17]). According to its supplier, the Class F fly ash contains major oxides of 52.9% SiO_2, 26.4 % Al_2O_3, 8.5% Fe_2O_3, and 2.1% CaO by mass, with a measured loss on ignition of 4.16% and measured strength activity indices (ASTM C311/ASTM C618 [18]) of 88% and 92% at 7 d and 28 d of age, respectively. Its density is reported as 2300 kg/m^3 by the manufacturer.

Three variables were selected as candidates for influencing the optimization of properties of cement/fly ash blends: cement PSD, fly ash PSD, and fly ash volumetric proportion percentage. Since the goal of this project was to evaluate the performance of "fine" cements blended with "coarse" fly ashes, the cement PSDs were characterized by their D_{90}[1] value while those of the fly ashes were characterized by their D_{10} value instead. Via grinding and classification, four cements with target D_{90} values of 7.5 μm, 10 μm, 15 μm, and 20 μm were obtained by Roman Cement and supplied to NIST, while four fly ashes with target D_{10} values of 5 μm, 10 μm, 15 μm, and 20 μm were also produced. The actual measured D_{90} values for the four cements were nominally 9 μm (designated as cement 10, see Tables 1 and 2), 11 μm (cement 9), 12 μm (cement 8), and 24 μm (cement 7), in contrast to the D_{90} of 36 μm for the original cement (cement 6). The actual measured fly ash D_{10} values were nominally 4 μm (fly ash 5), 11 μm (fly ash 4), 13 μm (fly ash 3), and 15 μm (fly ash 2) in contrast to 2.7 μm as measured for the original fly ash (fly ash 1). Finally, the four levels for the fly ash volume percentage were set at 20%, 35%, 50%, and 65%. These would correspond to fly ash mass fractions of 0.15, 0.278, 0.417, and 0.57, respectively. Since three variables with four levels implies 64 runs (4^3) for a complete factorial experiment, the number of experimental runs was reduced to 16 by applying a fractional factorial experimental design methodology [19]. The selected experimental design with both encoded-level (0, 1, 2, and 3) variables and original values is provided in Table 1. In addition to these sixteen mortar mixtures, three additional mixtures were investigated: (1) a control mixture produced with the original cement (two replicates prepared), (2) a 50:50 volumetric blend of the original cement and original fly ash as a reference point for the performance of an existing HVFA blend, and (3) a mixture containing 35% of an unprocessed (no grinding or subsequent classification) Class C fly ash (density of 2630 kg/m^3 and major oxides of 38.7% SiO_2, 19.2% Al_2O_3, 6.5% Fe_2O_3, and 23.5% CaO by mass, with a loss on ignition of 0.3%) with 65% of the cement 9 with a D_{90} of 11 μm, to investigate the influence of fly ash class on early and later age performance. The control and 50:50 reference mixtures were the first two to be prepared. Following this, the run order of the next 16 mixtures was randomized as shown in Table 1. After these sixteen mixtures were prepared, a replicate of the control mixture was executed. Finally, the mixture with 35% of a Class C fly ash was prepared and evaluated.

Table 2
PSD-estimated surface areas for the powder materials.

Cement or fly ash ID	PSD-estimated surface area (m^2/kg)
Class F fly ash 1 (D_{10} = 2.7 μm)	432
Class F fly ash 2 (D_{10} = 15 μm)	103
Class F fly ash 3 (D_{10} = 13 μm)	96
Class F fly ash 4 (D_{10} = 11 μm)	114
Class F fly ash 5 (D_{10} = 4 μm)	379
Cement 6 (D_{90} = 36 μm)	485
Cement 7 (D_{90} = 24 μm)	670
Cement 8 (D_{90} = 12 μm)	964
Cement 9 (D_{90} = 11 μm)	1017
Cement 10 (D_{90} = 9 μm)	1096

The PSDs of the original and processed cements and fly ashes were measured using a laser diffraction technique and are provided in Figs. 1 and 2, respectively. Based on these measured PSDs and assuming spherical particles, the cement and fly ash surface

[1] D_{90} indicates that 90% of the particles on a mass basis are below a given size (diameter) while D_{10} indicates that 10% of the particles on a mass basis are below a given diameter.

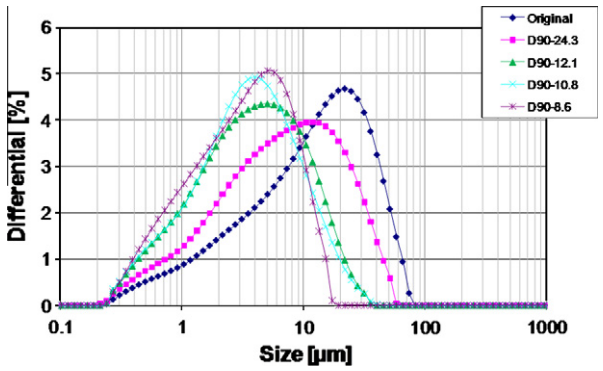

Fig. 1. Particle size distributions of the five cements shown as probability density functions. Each curve is the average of six individual measurements and the error bars (one standard deviation) would fall within the size of the shown symbols.

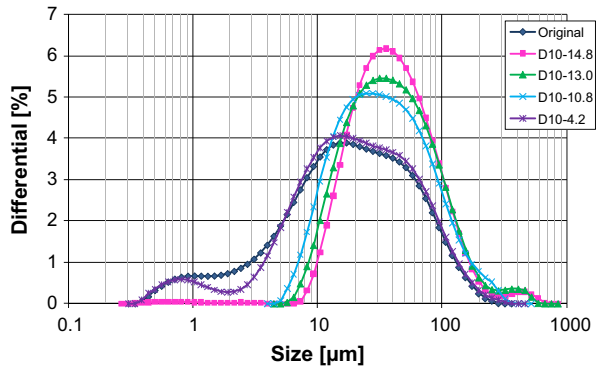

Fig. 2. Particle size distributions of the five Class F fly ashes shown as probability density functions. Each curve is the average of six individual measurements and the error bars (one standard deviation) would fall within the size of the shown symbols.

areas (Table 2) were calculated for each mortar mixture examined in the present study as a more quantitative variable than the targeted D_{90} or D_{10} values for representing the two powder components of the mixtures in subsequent regression analysis. In Table 2, it can be observed that the PSD-estimated surface area of 485 m^2/kg for the original cement 6 is significantly higher than its reported Blaine value of 376 m^2/kg, as the two measures are based on different principles.

Because the mortars were prepared with constant mixture volume fractions of water (0.24), sand (0.55), and binder (cement + fly ash, 0.21),[2] the addition of a HRWRA was necessary in some of the mixtures to maintain adequate flow and workability for specimen preparation. A polycarboxylate-type HRWRA known to produce minimal retardation was selected for this purpose. Screening studies were conducted by performing rheological measurements in blended cement pastes with various addition levels of the HRWRA to provide an estimate of the required dosage in mortar [16]. The so-determined HRWRA dosages employed in each mortar are included in Table 1. Regardless of the measured flow values, all mortar mixtures exhibited sufficient workability to mold mortar cubes for compressive strength testing and corrugated tubes for measurement of autogenous deformation (ASTM C1698 [18]). No HRWRA addition was required for either the control mixture (#1) or the reference 50:50 mixture (#2). For mortar mixture #19 prepared with 35% of the Class C fly ash, a HRWRA dosage of 0.67 g/100 g binder was employed. As would be expected, mixtures with

[2] The *w*/*c* of the control mortar was 0.35. For the 20%, 35%, 50%, and 65% mixtures, the corresponding *w*/*cm* on a mass basis were 0.365, 0.386, 0.406, and 0.427, respectively.

Table 3
Measured fresh properties of mortar mixtures.

Mortar mixture	Flow table value (%)	Air content (%)	Temperature (°C)
1 (Control)	114, 92.7	2.25, 2.32	23, 23
2 (50% original FA)	135	1.41	22
3 (35% FA 3 – Cem 7)	105	2.49	21
4 (50% FA 2 – Cem 7)	104	3.40	22
5 (35% FA 2 – Cem 8)	98	4.00	21
6 (50% FA 4 – Cem 9)	103	3.56	21
7 (65% FA 2 – Cem 10)	84.7	2.68	21
8 (35% FA 5 – Cem 9)	103	3.47	23
9 (20% FA 5 – Cem 10)	98	4.11	25
10 (35% FA 4 – Cem 10)	109	3.53	25
11 (65% FA 4 – Cem 8)	107	2.17	23
12 (50% FA 3 – Cem 10)	84.7	3.05	24
13 (20% FA 4 – Cem 7)	92	3.23	23
14 (20% FA 3 – Cem 8)	135	3.87	25
15 (65% FA 5 – Cem 7)	134	1.93	23
16 (50% FA 5 – Cem 8)	85.3	2.20	24
17 (20% FA 2 – Cem 9)	131	4.63	24
18 (65% FA 3 – Cem 9)	93.3	2.25	23
19 (35% C ash – Cem 9)	125	4.38	25

a higher cement content (lower fly ash proportion) or employing a finer cement required a higher dosage of the HRWRA to provide sufficient flow. For these dosages of HRWRA, the flows (ASTM C1437 [17]) measured on the various mortar mixtures are summarized in Table 3.

Each fresh mortar mixture was evaluated for air content via unit weight (cup) measurements according to ASTM C185 [17] and temperature (see Table 3), in addition to flow. Then, appropriate specimens were prepared for the following measurements:

(1) Isothermal calorimetry – the heat of hydration was measured during the course of 7 d on pre-mixed (as opposed to being mixed in situ in the calorimeter cells) sealed mortar samples with a mass of about 8 g using a TAM Air Calorimeter[3]; to provide an indication of variability, two specimens from the same batch were evaluated in neighboring calorimeter cells for each experiment,
(2) Semi-adiabatic calorimetry – the semi-adiabatic temperature was measured during the course of 3 d on a single sealed mortar specimen with a mass of approximately 330 g using a custom-built semi-adiabatic calorimeter unit [20]; replicate specimens from separate batches have indicated a standard deviation of 1.4 °C in the maximum specimen temperature during a 3 d test,
(3) Compressive strength – measured at 1 d, 3 d, 7 d, 28 d, 91 d, and 182 d on mortar cube specimens cured in a saturated calcium hydroxide solution, according to the procedures in ASTM C109 [17], but with a loading rate of 20.7 MPa/min, switching to deformation control (at the instantaneous deformation rate) once a stress of 13.8 MPa was reached; three specimens prepared from a single batch were evaluated at each time, with the averages and standard deviations provided in the results to follow, and
(4) Autogenous deformation – measured on triplicate or duplicate sealed mortar specimens prepared from a single batch, sealed in corrugated tubes according to the procedures in ASTM C1698 [18]; in the ASTM C1698 standard, the single laboratory precision is listed as 30 microstrain for mortar specimens.

[3] Certain commercial products are identified in this paper to specify the materials used and procedures employed. In no case does such identification imply endorsement by the National Institute of Standards and Technology, nor does it indicate that the products are necessarily the best available for the purpose.

Table 4
Measured mortar cube compressive strengths (means and standard deviations) for the 19 mortar mixtures at each of six different ages.

Mixture	Run Order ID	One-day mean strength, MPa psi (Std. dev.)	3-day mean strength, MPa psi (Std. dev.)	7-day mean strength, MPa psi (Std. dev.)	28-day mean strength, MPa psi (Std. dev.)	91-day mean strength, MPa psi (Std. dev.)	182-day mean strength, MPa psi (Std. dev.)
Control	1	36.7	54.4	63.6	80.3	84.7	86
		5320 (72)	7900 (340)	9220 (330)	11,640 (430)	12,280 (610)	12,470 (600)
Control repeat	1A	36.3	55.1	62.7	79.4	87.9	92.6
		5260 (180)	7990 (260)	9090 (580)	11,510 (430)	12,750 (510)	13,430 (490)
50% fly ash	2	13.6	21.3	29.3	49.1	70.6	79.5
		1980 (51)	3090 (73)	4250 (240)	7120 (160)	10,240 (240)	11,520 (510)
35% FA 3–Cem 7	3	27.4	39.7	51.8	69.7	79.2	90.9
		3980 (150)	5780 (130)	7380 (220)	10,100 (290)	11,480 (230)	13,170 (570)
35% FA 2-Cem 8	5	37.9	48	59.3	65.6	77.1	81.8
		5500 (210)	6960 (140)	8600 (250)	9510 (460)	11,180 (310)	11,860 (710)
35% FA 5-Cem 9	8	39	50.9	58.3	70	82.9	88.9
		5660 (210)	7380 (42)	8460 (220)	10,150 (170)	12,030 (280)	12,890 (580)
35% FA 4-Cem 10	10	44.6	53.4	64.8	72.4	80.6	83.3
		6460 (190)	7750 (370)	9400 (280)	10,500 (200)	11,690 (580)	12,080 (300)
35% C ash -Cem 9	19	38.8	51.4	61.4	79.6	85.9	90.9
		5620 (190)	7460 (140)	8910 (280)	11,540 (560)	12,450 (90)	13,180(1050)
50% FA 2-Cem 7	4	15.9	24.8	31.7	46.8	58.7	66.3
		2300 (130)	3600 (140)	4780 (170)	6790 (43)	8520 (38)	9620 (220)
50% FA 5-Cem 8	16	22.3	32.1	40.1	51.6	64.9	71.6
		3240 (100)	4660 (74)	5810 (140)	7480 (240)	9410 (460)	10,390 (600)
50% FA 4-Cem 9	6	22.7	31.8	38.3	47	56.2	65.1
		3300 (31)	4620 (85)	5550 (170)	6820 (220)	8160 (190)	9450 (200)
50% FA 3-Cem 10	12	25.2	33.7	40.7	49.4	57.6	63.3
		3650 (52)	4880 (200)	5910 (100)	7170 (260)	8360 (220)	9190 (430)
65% FA 5-Cem 7	15	8.4	14.6	18.3	30.5	47.7	57
		1210 (39)	2110 (44)	2660 (57)	4430 (200)	6910 (44)	8270 (370)
65% FA 4-Cem 8	11	10.2	14.7	18.8	27.3	38.1	49.4
		1480 (35)	2130 (73)	2720 (84)	3960 (70)	5530 (140)	7160 (370)
65% FA 3-Cem 9	18	10.2	14.8	19.1	25.7	35.7	46.2
		1480 (45)	2150 (48)	2770 (62)	3730 (69)	5180 (130)	6710 (250)
65% FA 2-Cem 10	7	11.7	15.9	19.2	26	33	41.8
		1700 (73)	2310 (42)	2780 (44)	3770 (21)	4790 (230)	6060 (80)
20% FA 4-Cem 7	13	36.7	50.8	63.5	78.1	89.8	91.8
		5320 (91)	7360 (220)	9220 (460)	11,330 (360)	13,020 (270)	13,310 (780)
20% FA 3-Cem 8	14	53.6	68.5	80.1	89.7	93.9	99.6
		7770 (84)	9940 (460)	11,620 (300)	13,010 (830)	13,620 (640)	14,440 (820)
20% FA 2-Cem 9	17	54.5	66.7	78.4	92.9	94.3	96.2
		7910 (330)	9680 (370)	11,370 (430)	13,470 (590)	13,680 (600)	13,960 (760)
20% FA 5-Cem 10	9	66.1	76.3	85.9	102	107	105
		9590 (250)	11,070 (210)	12,460 (270)	14,740 (570)	15,510 (890)	15,250 (370)

A subset of the mixtures (#1, #2, #8, #9, and #14) were evaluated with respect to setting time by performing ASTM C191 [17] measurements on cement pastes prepared in a high shear blender, but with the following modification to better prevent any evaporation from the specimen during the course of the test [21]. A moist sponge was held in place in the bottom of a foam cup using toothpicks, and the inverted cup placed on top of the truncated conical cement paste specimen, in an effort to maintain a near 100% relative humidity environment surrounding the hardening cement paste. The cup was removed prior to each measurement and returned immediately after recording the needle penetration. In addition to this, the mass of the specimen and its holder (conical mold and bottom plate) was determined at the beginning of the test and immediately after final set was achieved. Typical mass loss is less than 0.5% (specimen basis) even for specimens with final setting times of 8 h or more [21], indicating minimal evaporation during the course of the measurement. All set time measurements were conducted inside a walk-in environmental chamber maintained at 25.0 °C ± 1.0 °C. In the ASTM C191 standard [17], the single laboratory precisions are listed as 12 min and 20 min for initial and final times of setting, respectively.

3. Results and discussion

The compressive strength results for the mortar cubes evaluated at six ages for the nineteen mixtures are provided in Table 4. The results are grouped by fly ash volumetric percentage because, of the three investigated variables, this one had the largest influence on measured compressive strengths. In general, mixtures with 20% fly ash were able to develop compressive strengths that exceeded those of the control mixture at all six testing ages. Mixtures with 35% fly ash approached, and in a few cases equaled, the performance of the controls. Mixtures with either 50% or 65% fly ash provided compressive strengths that were significantly below those of the controls at all testing ages. It is worth repeating that all of these mixtures were prepared with the same volume fractions of water, sand, and binder powders.

For each testing age, linear regression analysis was conducted to determine the best-fit relationship between measured compressive strength for the sixteen mixtures (3–18) prepared according to the experimental design and the independent variables of fly ash volumetric percentage, cement surface area, and fly ash surface area. For each of the six compressive strength data sets, a good fit, with a correlation coefficient (R) greater than 0.97, was obtained. The so-determined regression coefficients along with the coefficients of determination (R^2) are provided in Table 5.

An alternative regression analysis was also completed based on the following model that employs the absolute surface areas of the cement and the fly ash in each specific mortar mixture:

$$\sigma(t) = A_t + B_t * \mathrm{CSA} * \rho_{\mathrm{cem}} * (1 - \mathrm{FA}/100) + C_t * \mathrm{FASA} * \rho_{\mathrm{FA}} * (\mathrm{FA}/100) + D_t * \mathrm{FA} \quad (1)$$

where $\sigma(t)$ is the compressive strength at time t, CSA is the cement surface area, ρ_{cem} is the specific gravity of the cement (3.2), FASA is the fly ash surface area, ρ_{FA} is the specific gravity of the fly ash (2.3), FA is the fly ash volume fraction in percent, and A_t, B_t, C_t, and D_t are the regression coefficients. The results of these regression analyses at each of the six ages are provided in Table 6. In general, this model provided slightly improved coefficients of determination relative to those obtained using only the three primary independent variables, particularly at early ages.

The following observations can be made based on the data in Table 4 and the results of the regression analyses based on the primary independent variables in Table 5:

(1) Fly ash volumetric proportion has a major influence on compressive strength values at all ages of testing. While the linear regression coefficients for fly ash content shown in Table 5 indicate a maximum magnitude of the (negative) coefficients at a testing age of 28 d, if these coefficients are normalized by the strength values of the control mortar at each age (as indicated by its values in Table 4), the relative influence of fly ash proportion is decreasing with age. This indicates that the longer one waits, the more the fly ash provides strength equivalence to cement, in agreement with general results from the literature.
(2) Cement fineness has a significant influence on strength at early ages, was deemed insignificant at a testing age of 91 d in Table 5, and once again produced a significant influence but of an opposite sign at 182 d in Table 5. Producing a finer cement accelerates hydration at early ages, contributing to strength enhancement, but at an age of 91 d, all of the cements investigated in this study were sufficiently fine to have nearly achieved complete hydration and thus provide nominally equivalent contributions to strength. Finally, at an age of 182 d, the finer cements produced slightly lower strengths. One possible explanation for this might be the superior micro-reinforcement provided by any remaining unhydrated coarser cement particles relative to their finer counterparts at this later age. Another would be that the higher temperatures produced during curing in the specimens based on the finer cements have contributed to lower long term strengths [10]. In support of this latter hypothesis, some of the mortars with 20% fly ash and using the finer cements did exhibit a higher maximum temperature in the semi-adiabatic tests than the control mortar.
(3) Conversely, for the Class F fly ash employed in this study, fly ash fineness, while insignificant at testing ages of 1 d, 3 d, and 7 d in Table 5, has a significant influence on strength at 28 d and beyond. Within the range of sizes investigated in the present study, coarser fly ash particles will not react as readily as finer ones, so that later age strength is best enhanced by utilizing finer fly ash particles.

For this particular combination of fly ash and cement, the regression analyses in either Tables 5 or 6 could be employed to engineer the desired compressive strength behavior of a mortar mixture. For example, given a specific fly ash surface area and desired volumetric substitution percentage, Eq. (1) could be solved to estimate the cement surface area that would be necessary to provide a desired strength development. This equation could be solved at 1 d and at 28 d, and the maximum so-determined cement surface area employed to assure compliance at both ages. Similarly, given fixed values of the cement and fly ash surface areas, Eq. (1) or the regression equation based on the primary independent variables (Table 5) could be solved to determine the maximum possible fly ash volumetric replacement that would provide the requisite strength values.

In terms of the goal of developing a fly ash blended cement that provides equivalent strength performance at ages of both 1 d and 28 d (at equal water contents), Table 4 suggests that three viable mixtures are mixture #8 prepared with 35% fly ash 5 and cement 9, mixture #13 prepared with 20% fly ash 4 and cement 7, and mixture #19 prepared with 35% of the Class C fly ash and cement 9. While the complete set of testing results for all 19 mortar mixtures have been included in reference [16], the remainder of this paper will examine how these three mixtures compare to the control mixture in terms of other early-age properties in addition to compressive strength.

Figs. 3 and 4 provide plots of the isothermal calorimetry instantaneous and cumulative heat measurements, respectively, for these four mixtures. The heat release curves suggest a slight retardation on the order of 2 h to 3 h for the fly ash blended cements when compared with the control pure portland cement mortar, as indicated by the time required to achieve a cumulative heat release of 50 J/cm^3 in Fig. 4, for example. The three mixtures with fly ash also exhibit a slightly different shape curve than the control mixture in Fig. 3, generally lacking the secondary shoulder on the right side of primary peak. This likely indicates that while the sulfate content of the cement had been optimized for the 100% pure portland cement system by the cement manufacturer, a different optimum sulfate level might be required for the blended mixtures.

The cumulative heat release curve for mixture #13 with 20% fly ash falls below that of the control mixture beyond 16 h of isothermal testing, while its measured compressive strengths at 1 d, 3 d, and 7 d are quite similar to those of the control mortar cubes in Table 4. A portion of this equivalent strength enhancement with reduced heat release is likely due to the finer cement being employed in the blended mixture. Previously, in 100% portland cement mortars, it has been noted that at equivalent heat releases, a finer cement produces considerably higher compressive strengths [9], likely due to its reduced interparticle spacing [9,22] concurrently decreasing the size of the flaws contributing to fracture. Additionally, this mixture contained the second finest of the four modified fly ashes (fly ash 4) and some of this fly ash may be contributing to the reactions even at early ages, with the strength produced per unit of heat generated being higher for the pozzolanic reactions than for the primary hydration reactions. These conjectures are further supported by the cumulative heat release curves for mixtures #8 and #19 where (nearly) equivalent strengths are

Table 5
Linear regression coefficients ± standard errors vs. age for compressive strength data for primary independent variables.

Age (d)	Intercept (MPa)	Cement surface area	FA content	FA surface area	Coefficient of determination (R^2)
Linear regression coefficients vs. age					
1	40.7 ± 6.8	0.0325 ± 0.0066	−0.957 ± 0.063	Not significant	0.952
3	61.6 ± 6.0	0.0279 ± 0.0058	−1.128 ± 0.056	Not significant	0.971
7	79.8 ± 5.5	0.0251 ± 0.0053	−1.302 ± 0.051	Not significant	0.981
28	103.7 ± 6.4	0.0120 ± 0.0060	−1.402 ± 0.058	0.0210 ± 0.0081	0.981
91	117.4 ± 2.2	Not significant	−1.289 ± 0.043	0.0341 ± 0.0060	0.986
182	124.2 ± 6.3	−0.0068 ± 0.0059	−1.122 ± 0.057	0.0276 ± 0.0080	0.971

Table 6
Linear regression coefficients ± standard errors vs. age for compressive strength data according to Eq. (1).

Age (d)	Intercept – A_t (MPa)	B_t	C_t	D_t	Coefficient of determination (R^2)
Linear regression coefficients vs. age					
1	12.9 ± 6.7	0.0194 ± 0.0022	0.0080 ± 0.0053	−0.407 ± 0.078	0.982
3	37.0 ± 5.0	0.0169 ± 0.0016	0.0105 ± 0.0040	−0.662 ± 0.058	0.992
7	58.0 ± 5.4	0.0151 ± 0.0017	0.0076 ± 0.0043	−0.878 ± 0.062	0.993
28	91.0 ± 9.1	0.0092 ± 0.0029	0.0154 ± 0.0072	−1.19 ± 0.11	0.983
91	112.6 ± 8.3	0.0036 ± 0.0027	0.0301 ± 0.0066	−1.302 ± 0.097	0.983
182	124 ± 10.	−0.0003 ± 0.0033	0.0259 ± 0.0081	−1.24 ± 0.12	0.967

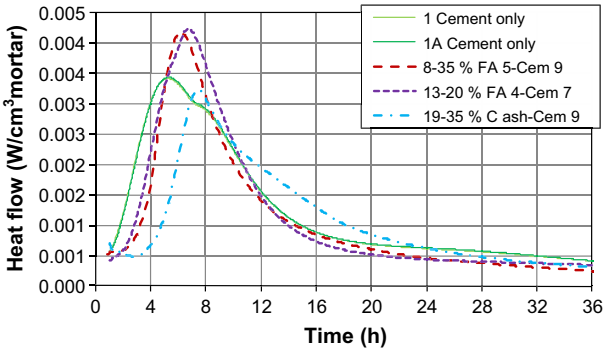

Fig. 3. Heat flow vs. time for mortars with similar strength development as that of the control mixture. Replicate measurements (that overlap one another) are shown for the control cement only mortar to provide an indication of variability.

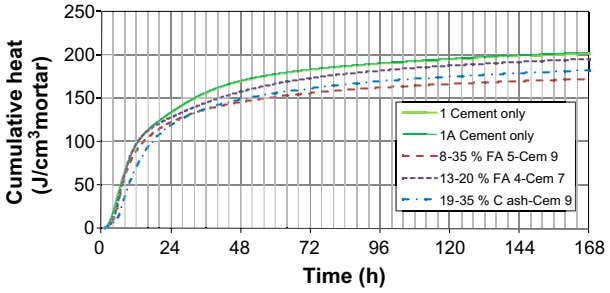

Fig. 4. Isothermal calorimetry curves showing cumulative heat release per cubic centimeter of mortar vs. time for mortars with similar strength development as that of the control mixture. Replicate measurements (that overlap one another) are shown for the control cement only mortar to provide an indication of variability.

obtained to those measured for the control mortars, but with substantially less cumulative heat release in Fig. 4. In agreement with previous experience with this particular Class C fly ash [14], the instantaneous and cumulative heat release curves for mixtures #8 and #19 indicate that the Class C fly ash, while contributing more to the initial retardation, is eventually more reactive than the Class F fly ash at early ages, as the cumulative heat release curve of mixture #19 exceeds that of mixture #8 after about 2 d. Likewise, the strength of the Class C fly ash mixture exceeds that of its Class F counterpart at ages of 3 d and beyond in Table 4.

Since isothermal calorimetry is a direct indication of the extent of the hydration reactions, but not of the setting process [23], a subset of the mortar mixtures were selected and their component pastes evaluated using the ASTM C191 standard test method for needle penetration [17]. Relative to the control mixture (#1), the results in Table 7 indicate both minor decreases in setting time (#9) and increases on the order of 1 h (#8, #14). For the subset of mixtures evaluated in this study, the most extreme delays in setting are observed for mixture #2, consisting of a 50:50 mixture of the original cement and original Class F fly ash. As mentioned for the extent of hydration in the previous section, the utilization of a finer cement helps to offset some of the delays in setting that are typically produced in HVFA mixtures.

The measured semi-adiabatic calorimetry temperature vs. time curves for the four mixtures are provided in Fig. 5. While mortar mixture #13 prepared with cement 7 and only 20% fly ash exhibited a semi-adiabatic response that was quite similar to those of the control mixtures, mixture #8 prepared with 35% fly ash 3 and cement 8 also provided a similar maximum temperature to that of the control, but followed by a more gradual cooling. Mixture #19 prepared with the Class C fly ash exhibited the greatest retardation, leading to a maximum temperature that was delayed by several hours and was several degrees lower than that of the control mortar, followed by a more gradual cooling. While exhibiting similar strength developments to the control mortar, these latter two 35% fly ash mixtures offer potential benefits with respect to reducing the propensity for early-age thermal cracking, via either their reduced maximum temperature or their reduced rate of cooling following this peak [8,24].

The measured autogenous deformation curves for the four mortars are provided in Fig. 6. For the control mortar, a slight expansion is observed during the first few days, followed by a shrinkage resulting in a total deformation of about 100 microstrain at 28 d. For the mixtures with either Class C or Class F fly ash and finer cements, this early-age expansion is not observed and the total shrinkage at 28 d is significantly increased, being on the order of 200 microstrain to 300 microstrain. In comparing mortar mixtures #8 and #19, switching from a Class F fly ash to a more reactive Class C fly ash increased the later age autogenous shrinkage at ages of 7 d and beyond, in agreement with the enhanced strength development in mortar #19 at these same ages in Table 4.

Table 7
Setting times (ASTM C191) of pastes from a subset of the mortar mixtures.

Paste/mortar ID	Fly ash (%)	Cement ID [D_{90}]	Fly ash ID [D_{10}]	Setting times (min)	
				Initial set	Final set
1	0	6 (36 μm)	–	168	214
2	50	6 (36 μm)	1 (2.7 μm)	258	318
8	35	9 (11 μm)	5 (4 μm)	227	267
9	20	10 (9 μm)	5 (4 μm)	131	168
14	20	8 (12 μm)	3 (13 μm)	220	255

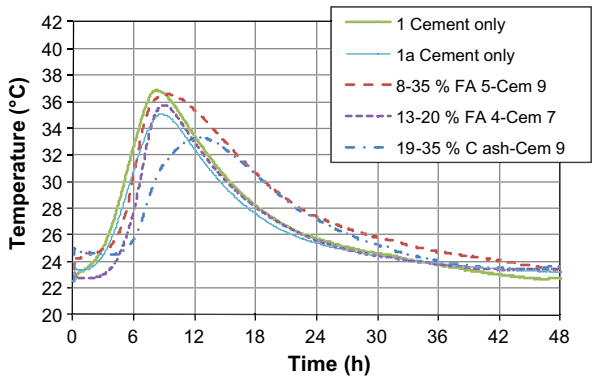

Fig. 5. Measured semi-adiabatic temperature vs. time for mortars with similar strength development as that of the control mixture.

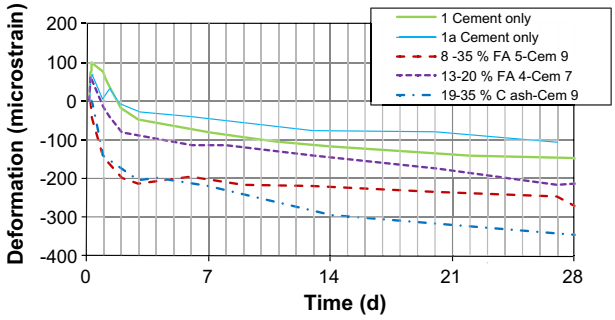

Fig. 6. Measured autogenous deformation vs. time for mortars with similar strength development as that of the control mixture.

Table 8
Measured 7-d and 28-d net autogenous deformations for mortars with similar strength development as that of the control mixture.

Mixture	7-d Net autogenous shrinkage (microstrain)	28-d Net autogenous shrinkage (microstrain)
1 – Cement only	182	247
1A – Cement only	115	175
8 – 35% FA 5 – Cem 9	202	269
13 – 20% FA 4 – Cem 7	178	279
19 – 35% C ash – Cem 9	220	348

Cusson has advocated that the autogenous cracking tendency of a mixture be characterized by the difference between the maximum (if any) expansion and the subsequent minimum deformation measured at a later age, such as 7 d or 28 d, for example [25]. Table 8 provides these 7-d and 28-d net autogenous deformation values for the four mixtures. These values indicate that the net deformations for mixture #13 with 20% fly ash and for mixtures #8 and #19 with 35% fly ash are slightly increased relative to those of the control mortars. If necessary, significant reductions in autogenous shrinkage can be achieved using a variety of readily available technologies including expansive additives, shrinkage-reducing admixtures, and internal curing [26]. Early-age (autogenous) cracking is just one of the myriad of durability concerns for cementitious materials; while it is expected that the durability performance of these HVFA mixtures will be equal (or perhaps superior) to that of their 100% portland cement counterparts, further research will be required to verify that this is indeed the case in field concretes.

4. Conclusions

The goal of engineering a blended cement with a substantial substitution of fly ash for cement, while maintaining both early-age and 28 d strengths at equivalent volumetric water fractions, has been achieved by the careful selection of cement and fly ash PSDs. Blending a finer cement with a coarser fly ash provides a needed boost to early-age strengths for the blended mixture, while maintaining an overall PSD that doesn't unduly increase the HRWRA demands. The present study indicates that, using this approach, volumetric substitutions on the order of 20% to 35% are feasible by processing readily available cements and fly ashes. These substitution levels should provide a significant contribution to the larger goal of producing sustainable concretes with reduced cement contents.

Compressive strengths could be adequately predicted using either a model based on the three independent variables examined in this study (cement surface area, fly ash surface area, and fly ash volume proportion) or a model that considers the absolute surface areas of cement and fly ash in each individual mortar mixture. These equations could be employed, for example, to estimate the maximum fly ash volumetric replacement for cement and fly ash with known surface areas.

Blended cement mortars that provided similar compressive strength development to the control mortar also provided generally similar performance with respect to other early-age properties, including heat release, semi-adiabatic temperature rise, and autogenous deformation. However, these blended mixtures did exhibit a minor retardation of up to several hours relative to the control 100% portland cement mortar.

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