TECH**BRIEF**

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# Evaluation of High-Volume Fly Ash Mixtures (Paste and Mortar Components) Using a Dynamic Shear Rheometer and an Isothermal Calorimeter

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This document is a technical summary of the unpublished Federal Highway Administration (FHWA) report, *Evaluation of High-Volume Fly Ash (HVFA) Mixtures (Paste and Mortar Components) Using a Dynamic Shear Rheometer (DSR) and an Isothermal Calorimeter*, available through the National Technical Information Service (NTIS).(1)

## Objective

The primary objective of this study was to develop a rationale for using a dynamic shear rheometer and an isothermal calorimeter as practical, quick scanning tools for the following purposes:

- Predict and assess early-age behavior of concrete mixtures containing different types and levels of cement and fly ash.
- Identify incompatible blends.
- Verify performance.

## Introduction

Many transportation experts in State transportation departments, the concrete industry, and academia are exploring ways to make concrete more sustainable and environmentally friendly. Supplementary cementitious materials (SCMs) such as fly ash, slag cement, and natural pozzolans have been used by many transportation agencies to achieve sustainability through the following features:

- Improved concrete performance and durability.
- Improved rheological properties (workability, finishability).
- Increased use of byproducts.
- Reduced carbon footprint associated with concrete production.
- Reduced overall cost of concrete.

Although the use of SCMs has increased steadily over the last two decades because of the benefits they afford, their use in highway applications still poses many unanswered questions. There is no sound, systematic protocol that can be used to routinely evaluate and proportion SCMs into concrete mixtures while ensuring that performance and durability are not compromised. Chemical, mineralogical, and granulometric characteristics of fly ash can vary from one source to another and within the same source. This variability in fly ash could have a profound impact on fresh and hardened properties of concrete.

Many transportation agencies have been using fly ash in their concrete pavement mixtures, with replacement levels ranging from 10 to 30 percent (typically 20 percent of the total cementitious material); however, these specifications are often based on empirical estimates that lack sound engineering evaluation. In an attempt to reduce the carbon footprint associated with cement production, reduce its adverse impact on the environment, and ultimately improve concrete performance, many transportation departments have expressed interest in using higher dosages of fly ash in concrete infrastructure.

While high-volume fly ash concrete can be proportioned to produce durable concrete, its use is not without problems. Some issues include slow strength gain at early ages, delayed setting, and reduced bleeding that results in extended curing time requirements and eventually slows down concrete paving during construction.

## Experimental Investigation

In the study, a total of 12 mortar mixtures and 14 paste mixtures were prepared. Two different Type I portland cements (low alkali and high alkali) and two different fly ashes (Class F and Class C) were used at three replacement levels (20, 40, and 60 percent). Table 1 shows a summary of the paste and mortar mixtures. A water-cementitious materials (w/cm) ratio of 0.40 was used for all the mixtures.

Mortar mixtures were mixed following ASTM C305, except for the mixer requirements.(2) Flow tests (ASTM C1437), modified unit weight using the base of the rollameter, setting time (ASTM C403), and compressive strength (ASTM C109) at the ages of 3, 7, 28, 56, 91, and 119 days were carried out.(3–5) Three cubes were tested at each age.

Paste mixtures were prepared according to ASTM C1738.(6) All materials were kept at 73 ±5 °F (23 ±3 °C) for at least 1 day before mixing the paste.

**Table 1. Mixtures in the experimental program.**

| Mixes | Fly Ash (percent) | Cement Type | Fly Ash Class |
|---|---|---|---|
| LA[1] | 0 | Low alkali | None |
| LA20F | 20 | Low alkali | Class F |
| LA40F | 40 | Low alkali | Class F |
| LA60F | 60 | Low alkali | Class F |
| LA20C | 20 | Low alkali | Class C |
| LA40C | 40 | Low alkali | Class C |
| LA60C | 60 | Low alkali | Class C |
| HA[1] | 0 | High alkali | None |
| HA20F | 20 | High alkali | Class F |
| HA40F | 40 | High alkali | Class F |
| HA60F | 60 | High alkali | Class F |
| HA20C | 20 | High alkali | Class C |
| HA40C | 40 | High alkali | Class C |
| HA60C | 60 | High alkali | Class C |

[1]Only paste mixtures prepared.

Isothermal calorimetry was performed at 77 °F (25 °C) for 72 h, following ASTM C1679.(7) Four replicates per mixture were run, with masses ranging from 0.157 to 0.169 oz (4.44 to 4.78 g). The heat of hydration was measured via a commercial eight-channel heat conduction isothermal calorimeter.

Rheological properties were tested following the procedure suggested by Ferraris and Obla at ages of 8, 30, 50, 70, and 90 min after the cement contacted water, except for mixture LA20F, which was tested only at 8, 30, and 50 min.(8) The tests were carried out at a controlled temperature of 77 ±0.4 °F (25 ±0.2 °C).

A parallel plate rheometer was used to determine yield stress and plastic viscosity. In order to avoid slippage, 1.4-inch (35-mm) serrated plates were used. A 0.02-inch (0.4-mm) gap was selected to represent the median distance between aggregates in concrete.(9) The shear rates selected ranged from 3 to 50 $s^{-1}$, following the Ferraris and Obla procedure.(8)

## Results and Discussion

### Fresh Properties

Table 2 shows the fresh property test results for mortar. Class C fly ash mixtures exhibited higher flow for all replacement levels and for both cements. The flow of mixtures containing Class C fly ash also increased with increasing fly ash content. This trend was not observed in Class F fly ash mixtures.

**Table 2. Fresh properties of mortars.**

| Mixes | Flow (percent) | Unit weight ($lb/ft^3$) | Initial setting (min) | Final setting (min) |
|---|---|---|---|---|
| LA20F | 94.5 | 139 | 214 | 311 |
| LA40F | 95.6 | 135 | 225 | 345 |
| LA60F | 88.1 | 132 | 232 | 363 |
| LA20C | 108.0 | 138 | 312 | 416 |
| LA40C | 125.7 | 137 | 423 | 562 |
| LA60C | 137.5 | 139 | 514 | 680 |
| HA20F | 99.5 | 136 | 205 | 302 |
| HA40F | 95.9 | 134 | 223 | 338 |
| HA60F | 84.8 | 131 | 247 | 421 |
| HA20C | 123.0 | 138 | 299 | 413 |
| HA40C | 138.0 | 138 | 422 | 567 |
| HA60C | 147.4 | 140 | 653 | 875 |

1 $lb/ft^3$ = 16.02 $kg/m^3$

For the same replacement level, mixtures containing Class C fly ash and high alkali cement presented a higher flow than the correspondent mixtures with low alkali cement. Again, this trend was not observed in Class F fly ash mixtures.

As expected, as the fly ash content increased, the initial and final setting times also increased, but this trend was even more pronounced in Class C fly ash mixtures.

## Compressive Strength

Figure 1 and figure 2 show the strength development over time. As expected, compressive strength decreased with an increase of fly ash content, and the decrease was more pronounced at early ages. Nevertheless, the compressive strengths achieved were quite high for replacements of 20 and 40 percent, reaching at least 3,000 psi (21,000 kPa), even at 3 days. There was little strength increase from 91 to 119 days.

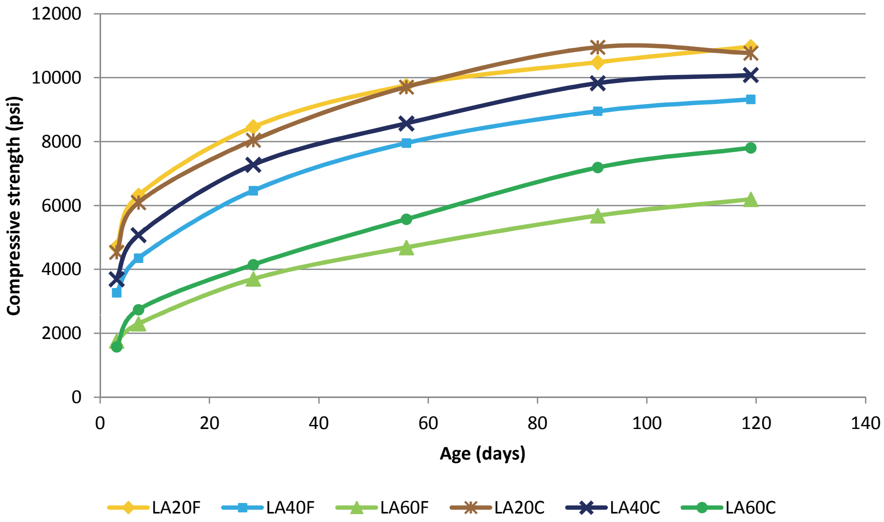
As shown in figure 1, mixtures containing low alkali cement with Class C fly ash yielded higher strengths, especially at longer ages, with the exception of mixtures containing only 20 percent fly ash. In mixtures containing high alkali cement, there was no significant difference in strength between mixtures with Class F fly ash and Class C fly ash at longer ages, as shown in figure 2.

## Calorimetry

A typical heat profile from isothermal calorimetry shows three peaks. An initial peak occurs immediately after mixing the water with the cementitious materials due to the rapid dissolution of $C_3A$ and initial formation of ettringite (AFt) phases. In the current experiment, this peak is not shown because the mixtures were prepared externally prior to insertion into the calorimeter. The second peak is related to the hydration of $C_3S$, and the third peak, also called the "sulfate depletion peak," corresponds to the reaction of $C_3A$. It has been suggested that the third peak relates to the renewed formation of ettringite.(10)

The heat flow over time is presented in figure 3 and figure 4 for low and high alkali cement, respectively. In the figures, LA is a mixture containing only low alkali cement and HA is a mixture containing only

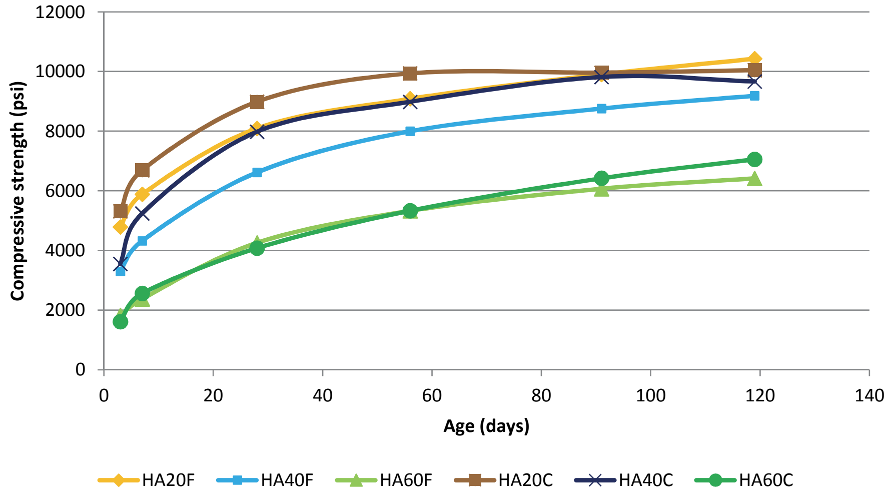
**Figure 1. Compressive strength development of mortar mixtures containing low alkali cement.**



1 psi = 6.89 kPa

high alkali cement. The substitution of cement by fly ash caused a dilution effect due to the fact that fly ashes are normally inert during the first few hours. As a consequence, the maximum heat flow decreased with increasing fly ash content, and in some cases, there was retardation in the heat flow. For the same mass replacement, Class C fly ash mixtures yielded higher degrees of retardation than Class F fly ash mixtures; although the volume of Class C fly ash for the same mass was slightly lower due to its higher specific gravity. Similar behavior was observed by Bentz when using fly ashes from the same sources.(11)

**Figure 2. Compressive strength development of mortar mixtures containing high alkali cement.**



1 psi = 6.89 kPa

**Figure 3. Heat flow of mixtures containing low alkali cement obtained through isothermal calorimetry.**

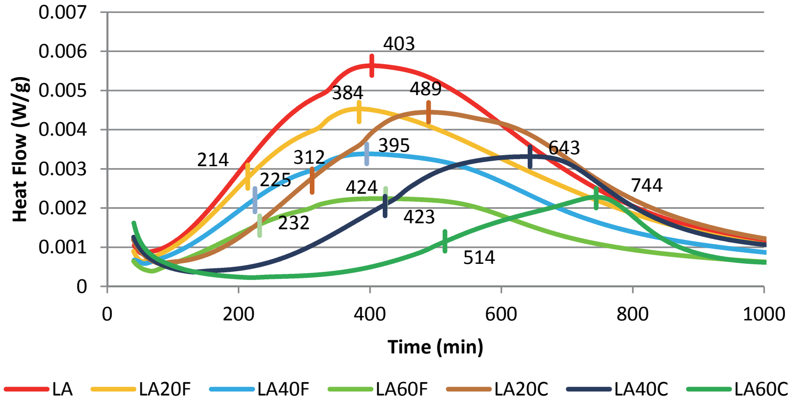
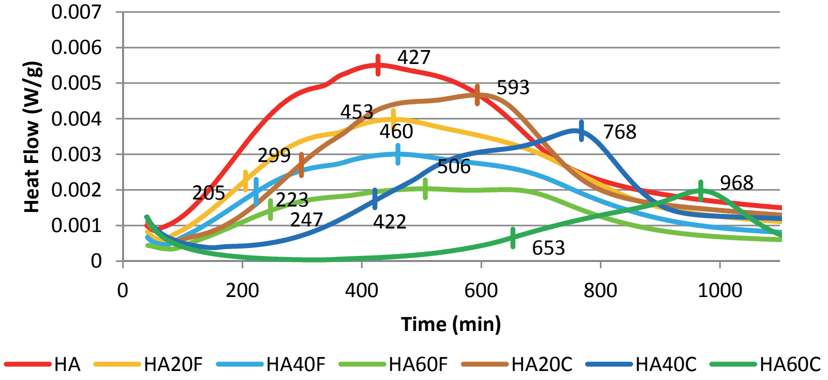


**Figure 4. Heat flow of mixtures containing high alkali cement obtained through isothermal calorimetry.**



A small fourth peak can be observed in mixtures containing Class C fly ash. This peak increases with the increase in fly ash content and occurs between 22 and 23 h. This peak has been attributed to the hydration of $C_4AF$ as well as the conversion of AFt to the AFm phase.(12) However, in the present study, this peak was found to increase with the increase of Class C fly ash. Consequently, it was concluded that either the fly ash promotes the hydration of the cement and serves as a nucleation site for the cement hydration (and more specific to the hydration of $C_3A$), or the pozzolanic reaction of the fly ash could manifest itself in the fourth hydration peak.(12) This peak appears slightly bigger with mixtures containing low alkali cement, which has a lower $C_3A$ content and a higher $C_4AF$ content than the high alkali cement.

The curves for the high alkali cement mixtures shifted to the right, indicating a delay compared to the low alkali cement mixtures. The delay on the maximum heat flow varied from 24 min for plain mixtures to 223 min for mixtures containing 60 percent Class C fly ash. The difference between low alkali and high alkali cement mixtures containing Class F fly ash was less pronounced, ranging from 69 to 83 min.

In each curve shown in figure 3 and figure 4, with the exception of the mixtures containing only cement, two markers are shown. The first represents the initial set time of the respective mortar mixture, and the second represents the time of the maximum heat flow. In figure 5, these two markers are plotted against each other, correlating the time of maximum heat flow of pastes and the initial setting time of the mortars containing the same proportions of cementitious materials and the same w/cm ratio. There is a very good correlation ($R^2 = 0.93$), indicating that calorimetry measurements can be used to predict the initial setting time. A similar correlation was obtained between final setting time and time of the maximum heat flow ($R^2 = 0.92$). This shows that isothermal calorimetry can be used as a surrogate test for setting time (ASTM C403), a laborious test to identify incompatibilities.(4) It is important to emphasize that the linear regression in figure 5 remains to be validated for different w/cm ratios and different cements and fly ashes.

In a study on incompatibility of combinations of concrete materials, Taylor et al. suggested a test protocol where a combination of materials would be considered incompatible when the time of maximum heat flow is delayed by more than 60 min.(13) According to the criteria presented by Taylor et al., only mixtures LA20F, LA40F, LA60F, HA20F, and HA40F would be considered compatible.(13) All the mixtures containing Class C fly ash would be considered incompatible.

**Figure 5. Relation between time of maximum heat flow of pastes and initial setting time of respective mortar.**

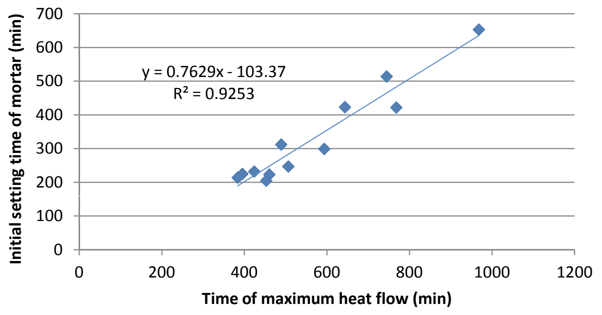
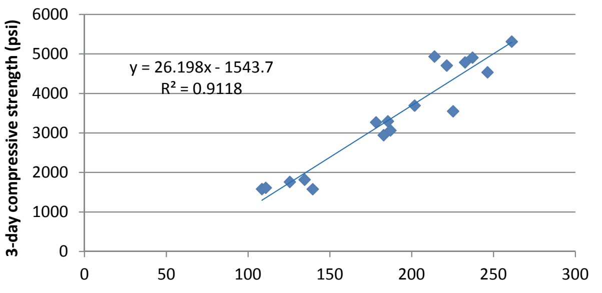


**Figure 6. Relation between cumulative heat for the first 72 h of hydration of pastes and 3-day compressive strength of respective mortars.**



1 psi = 6.89 kPa

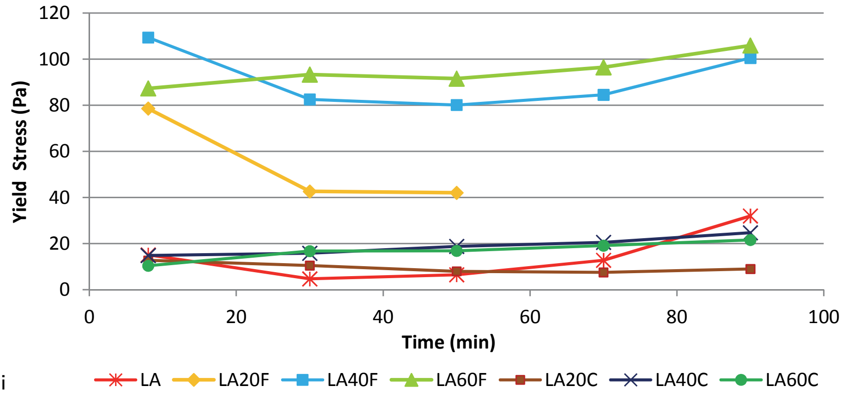
Figure 6 shows the relation between the cumulative heat for the first 72 h of paste hydration and the 3-day compressive strength of mortar cubes made with the same cementitious proportions and w/cm ratios. It is important to emphasize that the linear regression in figure 6 needs to be validated for different w/cm ratios and different cements and fly ashes. Nevertheless, isothermal calorimetry appears to be a reliable screening tool for selecting mixture proportions.

## Rheology

Figure 7 and figure 8 present the yield stress of mixtures at 8, 30, 50, 70, and 90 min, and figure 9 and figure 10 present the plastic viscosity.

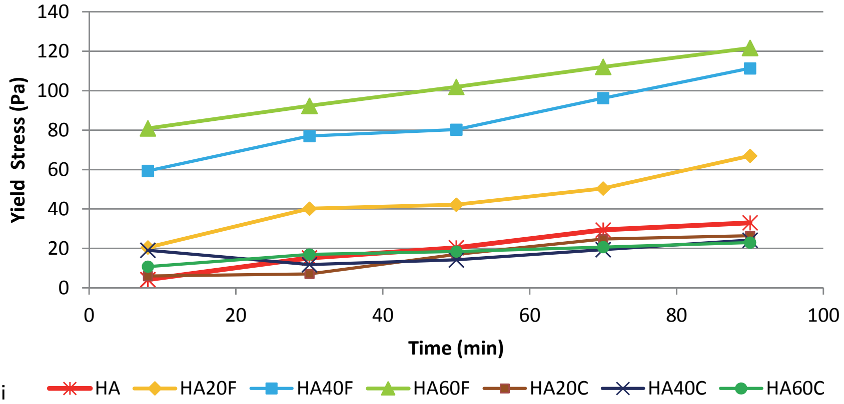
For mixtures containing Class F fly ash, both the plastic viscosity and the yield stress increased with increasing fly ash content, with the exception of mixture LA60F at 8 min. For mixtures containing Class C fly ash, this trend was not observed, mainly

**Figure 7. Yield stress over time of mixtures containing low alkali cement.**



1 Pa = 1.45 × $10^{-4}$ psi

**Figure 8. Yield stress over time of mixtures containing high alkali cement.**



1 Pa = 1.45 × $10^{-4}$ psi

because both plastic viscosity and yield stress were very low and differences between mixtures were small and within the variability of the test.

When comparing mixtures using Class F fly ash with those made with Class C fly ash, the Class F fly ash mixtures yielded higher plastic viscosities and much higher yield stresses at all levels of cement replacement. It should be noted that the Class F fly ash used in this study was much coarser than the Class C fly ash. Figure 7 through figure 10 also show that the yield stress and plastic viscosity of the mixtures that presented considerable setting delays (mixes LA20C, LA40C, LA60C, HA20C, HA40C, and HA60C) did not change considerably over time.

Figure 11 shows the relationship between the flow of mortars and the yield stress of pastes. The graph shows higher flows with lower yield stresses, but no good correlation was found. Nevertheless, it appears that yield stress measurement may be a better tool to differentiate mixtures exhibiting low flows (below 100 percent), whereas the flow test may be a more appropriate technique for differentiating mixtures with low yield stresses (below 0.0029 psi (20 Pa)).

## Conclusions

From the results presented, the following conclusions can be made:

- For the materials used in this study, Class F fly ash did not significantly affect setting time, even at 60 percent cement replacement. The compressive strength of mixtures with up to 40 percent replacement was found to be satisfactory at 3 days.
- For the materials used in this study, Class C fly ash significantly affected setting time, even at 20 percent cement replacement. Mixtures containing high alkali cement were affected to a greater level. The 3-day compressive strength of mixtures with up to 40 percent replacement was found to be satisfactory.
- For the materials used in this study, mixtures containing Class C fly ash gave rise to higher flow, lower yield stress, and lower plastic viscosity.

Figure 9. Plastic viscosity over time of mixtures containing low alkali cement.

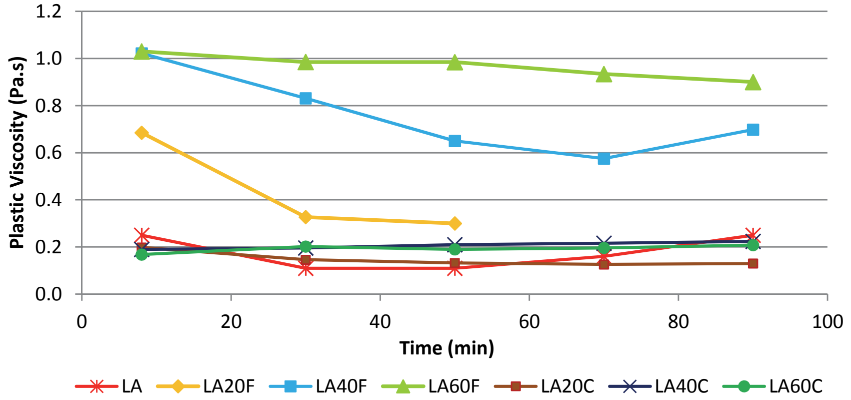
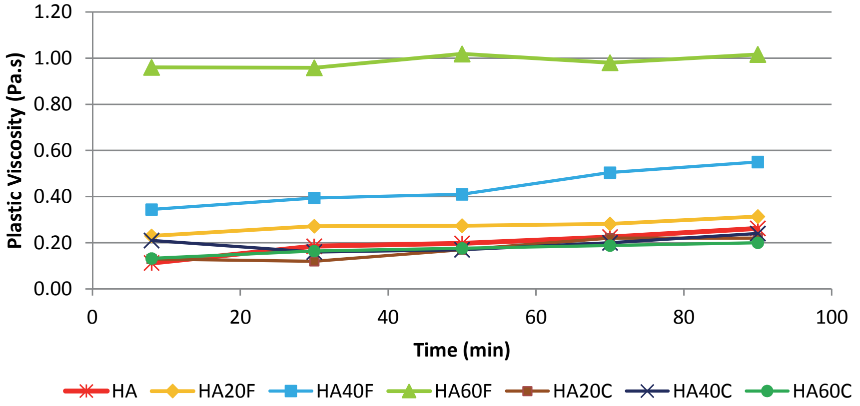
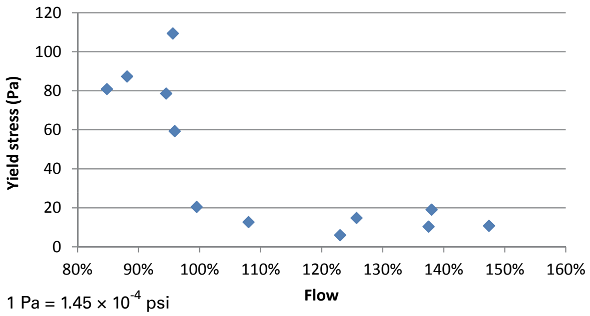


Figure 10. Plastic viscosity over time of mixtures containing high alkali cement.



- Isothermal calorimetry was confirmed to be a good screening tool to detect incompatibilities (when related to delayed setting time) and can be used for setting time and compressive strength prediction at early ages.
- The rheological methodology used in this study can give an indication of setting delay, since neither yield stress nor plastic viscosity of the mixtures exhibiting setting delays changed significantly over time.

Figure 11. Relation between flow and yield stress.



1 Pa = 1.45 × $10^{-4}$ psi

## References

1. Tanesi, J., Ardani, A., Meininger, R., and Nicolaescu, M. (2012). *Evaluation of High-Volume Fly Ash (HVFA) Mixtures (Paste and Mortar Components) Using a Dynamic Shear Rheometer (DSR) and Isothermal Calorimeter*, Report No. PB2012-112546, National Technical Information Service, Springfield, VA.
2. ASTM C305. (2006). *Standard Practice for Mechanical Mixing Hydraulic Cement Pastes and Mortars of Plastic Consistency*, ASTM International, West Conshohocken, PA.
3. ASTM C1437 (2007). *Standard Test Method for Flow of Hydraulic Cement Mortar*, ASTM International, West Conshohocken, PA.
4. ASTM C403/C403M (2008). *Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance*, ASTM International, West Conshohocken, PA.

5. ASTM C109/C109M (2008). *Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or 50-mm Cube Specimens)*, ASTM International, West Conshohocken, PA.

6. ASTM C1738 (2011). *Standard Practice for High-Shear Mixing of Hydraulic Cement Paste*, ASTM International, West Conshohocken, PA.

7. ASTM C1679 (2009). *Standard Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry*, ASTM International, West Conshohocken, PA.

8. Ferraris, C. and Obla, K. (2001). "Influence of Mineral Admixtures on the Rheology of Cement Paste and Concrete." *Cement and Concrete Research*, Vol. 31, No. 2, pp. 245–255.

9. Ferraris, C. (1999). "Measurement of the Rheological Properties of Cement Paste: A New Approach." *International RILEM Conference on the Role of Admixtures in High Performance Concrete*, RILEM, Monterrey, Mexico.

10. Baert, G., Van Driessche, I., Hoste, S., De Schutter, G., and De Belie, N. (2007) "Interaction Between the Pozzolanic Reaction of Fly Ash and the Hydration of Cement." *Proceedings of the 12th International Congress on the Chemistry of Cement*, International Congress on the Chemistry of Cement.

11. Bentz, D. (2010). "Blending Different Fineness Cements to Engineer the Properties of Cement Based Materials." *Magazine of Concrete Research*, 62(5), pp. 327–338.

12. Lagier, F. and Kurtis, K. (2007). "Influence of Portland Cement Composition on Early Age Reactions with Metakaolin." *Cement and Concrete Research*, 37, pp. 1411–1417.

13. Taylor, P., Johansen, V., Graf, L., Kozikowski, R., Zemajtis, J, and Ferraris, C. (2006). *Identifying Incompatible Combinations of Concrete Materials: Volume II-Test Protocol*, Report No. HRT-06-080, Federal Highway Administration, McLean, VA.

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**Key Words**—Fly Ash, Rheology, Calorimetry, Incompatibility.

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