Accepted by ACI Materials Journal (03/10)

Powder Additions to Mitigate Retardation in High Volume Fly Ash Mixtures

Dale P. Bentz
Building and Fire Research Laboratory
National Institute of Standards and Technology
100 Bureau Drive Stop 8615
Gaithersburg, MD 20899-8615 USA
E-mail: dale.bentz@nist.gov

Abstract

While high volume fly ash (HVFA) concrete mixtures are attractive from a sustainability viewpoint, they are sometimes plagued by long delays in finishing, producing a performance that is unacceptable to contractors. In this paper, isothermal calorimetry studies are conducted to examine excessive retardation in HVFA mixtures based on both Class C and Class F fly ashes. In addition to quantifying the retardation, the calorimetric curves are also used to evaluate the performance of mitigation strategies based on various powder additions. Powder additions examined in the present study include an aluminum trihydroxide, calcium hydroxide, cement kiln dust, condensed silica fume, limestone, and a rapid set cement. The addition of either 5 % calcium hydroxide or 10 % of the rapid set cement by mass of total solids (powders) is observed to provide a significant reduction in the retardation measured in mixtures based on either class of fly ash, for the material combinations examined in this study. Thus, these two powder additions may provide viable solutions to mitigating excessive retardation, extending the utilization of HVFA mixtures in practice.

Keywords: Building technology; high volume fly ash; hydration; isothermal calorimetry; retardation; sustainability.

Introduction

Sustainability looms as a major consideration for the concrete industry in the coming years.[1] Cutting CO_2 emissions per unit volume of concrete placed is consistently viewed as one major emphasis of the sustainability movement, and high volume fly ash (HVFA) concrete mixtures are viewed as one potential solution to providing a significant emissions reduction.[2] While more HVFA mixtures are being employed in practice, a common remark from end users is that for some applications, excessive retardation often significantly delays finishing operations. In extreme cases, subsequent early age strengths may be inadequate to achieve engineering and design objectives such as timely formwork removal. The complexity of this problem is well recognized by both laboratory and field personnel, with its likelihood dependent on environmental conditions, material combinations, and material variability.[3,4]

In an ongoing study at the National Institute of Standards and Technology (NIST), a series of mortars with 50 % fly ash replacement for cement by mass are being evaluated for a series of early-age properties and strength development out to 1 year. Mixtures prepared with either a Class C or a Class F[5] fly ash are being investigated, along with the utilization of a Type III cement[6] (in addition to the control Type II/V cement). The retardation problem mentioned above is well demonstrated by the isothermal calorimetry results obtained for a subset of these mortars, as provided in Figure 1. Results in Figure 1 are plotted both on a per gram of solids (left, including cement, fly ash, and any added gypsum) and on a per gram of cement (right) basis. The former normalization is dominated by the dilution effects of a 50 % replacement of reactive cement with less reactive fly ash, while the latter is conventionally employed in the literature and provides a better view of the inherent reactivity of the cement in the mixture. It can be seen in Figure 1 that while the control ordinary portland cement mortar with a water-to-cementitious materials ratio (*w/cm*) of 0.3 begins to liberate substantial energy about 4 h after mixing, for the mortars prepared with either the Class C or the Class F fly ash, this liberation is delayed until beyond about 8 h. Similar retardations with lower (20 %) replacement levels of fly ash have been observed previously, particularly for Class C ashes.[3] It should be noted that the polycarboxylate high range water reducing agent (HRWRA, 43 % solids, with a specific gravity of 1.08) dosage was adjusted to provide acceptable workability for each mortar mixture; its possible retardation effects are thus confounded with those of the fly ashes, as will be explored in more detail later. While it was found that switching to a Type III cement could increase 1 d mortar cube compressive strengths by about 60 % (roughly from 17.2 MPa or 2500 psi to 27.6 MPa or 4000 psi),[7] the reduction that they produced in this initial retardation was minimal, being less than 1 h (Figure 1). Thus, while the Type III cement successfully mitigates the reduction in early-age strength,[7] it does little to reduce the excessive retardation experienced in these mixtures. Of course, hydration does not typically occur under isothermal conditions in the field, so semi-adiabatic calorimetry measurements[8,9] were executed as well. The results in Figure 2 once again indicate significant retardation on the order of 4 h for the HVFA mixtures relative to the control mortar. In Figure 2, the significantly reduced maximum temperature produced in the HVFA mortar mixtures is also worthy of note; such a reduction may lead to a reduced tendency for early-age cracking, due to thermal stresses for example.[7] Figures 1 and 2 clearly illustrate a significant delay in early hydration for the HVFA mixtures. In the present study, further calorimetric measurements have been employed to explore potential solutions for mitigating this retardation. As opposed to employing additional liquid chemical admixtures, the focus of the considered mitigation strategies has been limited to powder additions to the HVFA mixtures.

Research Significance

For the use of HVFA mixtures to become the norm in the 21st century, robust and predictable early-age performance must be assured. This study investigates various powder additions to paste mixtures that may prove useful in providing these features in systems that have exhibited significant retardation in hydration and delays in finishing time. These mitigation strategies may serve as additional tools in the contractor/supplier toolbox for delivering a consistent high quality, sustainable concrete. The scope of the present study is to provide a screening tool based on calorimetry for identifying promising powder additions to mitigate this excessive retardation; measurements of setting and rheology, as well compressive strength are being addressed in follow up studies.[7,10]

Materials and Experimental Methods

The measured particle size distributions (PSDs) for the cement, the two classes of fly ash, and the powder additions investigated in this study are provided in Figure 3, except for the aluminum trihydroxide powder which was coarser than the other powders, having a modal particle diameter of 85 µm (0.0033 in) and containing no particles smaller than 20 µm (0.00079 in) in diameter. A Type II/V cement (5 % C_3A content) was employed; its detailed chemical composition as provided by the manufacturer is listed in Table 1, and a variety of its early-age performance properties have been published recently.[9] The Blaine fineness of the Type II/V cement is 387 m^2/kg, as supplied by the manufacturer, and its specific gravity is 3.250. A supply of a Class C fly ash (specific gravity of 2.690) was obtained from a concrete ready-mix producer and a Class F fly ash (specific gravity of 2.100) from a local fly ash producer. Detailed oxide compositions for the two fly ashes, as determined at a private testing laboratory, are also provided in Table 1.

Condensed silica fume (CSF) in undensified dry powder form was obtained from a chemical admixture supplier. Cement kiln dust (CKD) with a chemical composition as given in Table 1 was obtained from a local cement manufacturer. Limestone powder (93.5 % $CaCO_3$)

and a rapid set cement (mainly a mixture of calcium sulfoaluminate, dicalcium silicate, and gypsum) were obtained from commercial suppliers. The manufacturer-supplied chemical composition of the rapid set cement is included in Table 1. An aluminum trihydroxide (hydrate) powder (designated as C30, 65 % Al_2O_3) was obtained from an aluminum manufacturer. Calcium hydroxide and calcium sulfate dihydrate (gypsum, 98 % purity) were purchased from an international chemical company. As mentioned previously, the HRWRA was of the polycarboxylate type and was obtained directly from a chemical admixture supplier.

For each examined paste, all powder ingredients, with a typical mass of 60 g (0.13 lb), were first pre-blended for 30 min in a sealed plastic jar on a Turbula[1] blender. Mixing with water was performed by hand (kneading) in a sealed plastic bag for two minutes. This mixing procedure was chosen mainly due to the small batch sizes required for the calorimetry experiments. While it is well recognized that mixing intensity can significantly influence early age hydration and setting, it will be seen that the hand-mixed paste mixtures prepared in this study exhibited similar retardation characteristics as the mortars shown in Figures 1 and 2, prepared using a planetary mixer. When employed in these paste mixtures, the HRWRA was pre-mixed with the mixing (distilled) water.

In this study, isothermal calorimetry was employed as the screening tool to identify powder additions with the potential to mitigate the excessive retardation in HVFA mixtures. Isothermal calorimetry measures the rate of heat release from a hydration mixture due to the ongoing chemical reactions and has been extensively employed for examining cement/admixture interactions and identifying material problems and potential mitigation strategies.[3,4] Generally, isothermal calorimetry was conducted for a period of 7 d using single or replicate paste

---

[1] 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, nor does it indicate that the products are necessarily the best available for the purpose.

specimens with a mass of 5.6 g (0.012 lb). The prepared paste was first placed in the glass calorimeter specimen vials and then loaded into the calorimeter, so that the initial "mixing" peak was not examined in this study. Unless otherwise indicated, pastes were prepared with *w/cm* = 0.3.

Results and Discussion

Potential Contribution of Dilution Effect

Since a 50 % replacement of cement by fly ash doubles the effective water-to-cement ratio (*w/c*) of the mixture, preliminary calorimetry studies were conducted to determine the influence of *w/c* on the heat release curves for the Type II/V cement. The results in Figure 4 indicate that while a small retardation (≈ 1 h) is produced as the *w/c* is increased from 0.3 to 0.6, this dilution effect is clearly not responsible for the major part of the retardation observed in Figure 1.

Optimum Gypsum Addition for 50 % Class C Fly Ash Mixture

The potential for high levels of Class C fly ash replacement for cement to disturb the sulfate balance of hydrating mixtures is well known.[3,4,11] In the present study, this effect was first noted when the mortar cubes produced with 50 % Class C fly ash and no additional calcium sulfate produced a 1 d compressive strength of only 6.0 ± 0.1 MPa (870 psi, standard deviation for three cubes is reported). Following this, pastes were produced with various addition levels of calcium sulfate dihydrate (gypsum) between 1 % and 5 % (of total mass of cementitious materials including gypsum), but no HRWRA. Based on the calorimetry results in Figure 5 and similar curves generated for the Type III cement, a 2 % addition level of gypsum was chosen for all future studies employing the Class C fly ash; this addition level increased the 1 d mortar cube compressive strength to a more acceptable level of 16.1 ± 0.2 MPa (2330 psi). The influence of the sulfate additions is as expected,[4] with the greater addition levels causing a significant shift to later times for the 2nd hydration peak that is related to sulfate depletion and renewed aluminate hydration. While the sulfate additions increase early age hydration (and strength), it is critical to note that in Figure 5, regardless of the sulfate addition level, a 4 h retardation with respect to the control (cement only) paste is consistently produced. Thus, the sulfate additions are a necessary measure to ultimately produce “normal” hydration and strength development in the mixture with 50 % Class C fly ash, but unfortunately, they do little to mitigate this mixture’s excessive retardation, for the materials examined in this study.

Separation of Effects of HRWRA and Fly Ash Replacements on Retardation

For *w/cm* = 0.3 paste mixtures, all combinations of a two-level design (with/without) for fly ash and HRWRA as variables were examined for both the Class C and the Class F fly ash. For each mixture with HRWRA, the HRWRA dosage was set at the level observed to provide sufficient workability in mortar mixtures. Calorimetry results are summarized in Figure 6, with separate plots for each class of fly ash. It can be clearly observed that in the case of the 50 % Class C fly ash paste, both the fly ash itself and the HRWRA contribute to the observed retardation, with the retardation produced when both are used being greater than either individually. This increase in retardation when both are added to the mixture is in spite of the fact that the addition of the Class C fly ash allowed for a favorable 50 % reduction in the HRWRA dosage required to provide adequate workability in mortars as indicated in Figure 6 (top).

Conversely, for the Class F fly ash, the fly ash itself didn’t cause significant retardation. However, due to the PSD and lower specific gravity of the class F fly ash, to produce a mortar with sufficient workability required an increase in the HRWRA dosage from 0.67 % to 0.87 %

per mass of cementitious material, with a concurrent and dramatic increase in retardation as indicated in Figure 6 (bottom). A robust powder addition should optimally be able to aid in reducing the retardation for both classes of fly ash without impacting initial slump and workability. It should be noted that, while beyond the scope of the present study, for the Class F fly ash mixture, an alternative approach for mitigating the excessive retardation would be to seek out a different HRWRA that provides sufficient workability without adversely affecting hydration.

Screening of Powder Additions in 50 % Class C Fly Ash Mixtures

Preliminary efforts were directed towards mitigating the excessive retardation in the mixtures containing the Class C fly ash. As seen in Figure 7, a variety of powder additions were examined for their ability to restore the main hydration peak to the time observed for the control cement paste with no fly ash. At the 5 % level (mass of total solids), limestone powder was observed to have minimal effect on the hydration response, in agreement with previous results.[12] The 10 % C30 aluminum trihydroxide mixture slightly increased the heights of the hydration peaks, particularly the second peak related to renewed aluminate hydration, but had minimal effect on accelerating their occurrence. The 10 % CKD only minimally accelerated the occurrence of the hydration peaks, but did significantly increase the early-age (1 d) hydration, as indicated by the increased area under the hydration peak(s) in Figure 7. Of the powder additions examined in Figure 7, the 5 % CSF had the most favorable results, accelerating the hydration by slightly more than 1 h, but falling short of restoring the hydration to the conditions observed with the control cement paste with no fly ash replacement. Silica fume has been successfully employed in the past to compensate for the reduced mechanical properties of HVFA concretes,[13] but its influence at the very early ages of relevance to setting and finishing operations is perhaps more limited, as indicated in Figure 7.

Two other powder additions that did exhibit a marked degree of success in mitigating the retardation were calcium hydroxide and a commercially available rapid set cement. Calorimetry results for these systems are presented in Figure 8. Roberts and Taylor[4] have pointed out that for early hydration, when "there is insufficient calcium in solution because it has been consumed in early C_3A hydration, silicate hydration will slow or stop, leading to retardation of the concrete or failure to set." To verify this conjecture, additional calcium in the form of calcium hydroxide was added to the Class C fly ash mixture. One might consider that calcium is already being supplied to solution via the addition of 2 % gypsum to this mixture, but the reality is more likely that both the calcium and sulfate supplied by this additional gypsum are participating in aluminate (not silicate) reactions, leading to the formation of ettringite, for example. Conversely, calcium hydroxide should supply calcium (and hydroxide) ions to the pore solution without providing an additional sulfate source. Indications in Figure 8 are that a 5 % calcium hydroxide addition is indeed effective in mitigating the excessive retardation of the 50 % Class C fly ash paste, shifting the primary hydration peak back close to that of the control paste without fly ash. Thus, further studies were conducted to examine its effectiveness in both fly ash mixtures when the HRWRA is present in its required dosages, as will be described subsequently.

The rapid set cement was also effective in reducing the excessive retardation in the high volume Class C fly ash mixture. The rapid set cement contains a calcium sulfoaluminate phase, dicalcium silicate, and gypsum and has a hydration chemistry distinct from that of ordinary portland cement. It was hypothesized that its chemistry might not be significantly retarded by the fly ash, thus contributing to a viable three component blend in which the rapid set cement contributes to the very early reactions and strength development, the ordinary portland cement to the early and intermediate reactions, and the fly ash to the long term performance. The results in Figure 8 indicate that the rapid set cement holds promise in this regard, at either the 10 % or 20 % replacement level. For further studies to be described subsequently, the 10 % level was selected, as it was feared that with the 20 % replacement level, the very early hydration might be excessive and lead to too rapid a setting of the mixture for this application. As with the calcium hydroxide, this preliminary favorable performance was further evaluated for both fly ashes with requisite HRWRA dosages.

Calcium Hydroxide Additions in Detail

Examining the calcium hydroxide addition in more detail, first, the influences of calcium hydroxide additions on the hydration response of ordinary portland cement pastes with and without HRWRA were examined. The results, presented in Figure 9, indicate that for these $w/cm = 0.3$ pastes, the replacement of 5 % of the cement by calcium hydroxide provides about 1.5 h of acceleration and also slightly increases the area under the hydration peak curve. This effect is more pronounced when a HRWRA is present in the mixture, with an acceleration of slightly more than 2.5 h relative to the mixture with no additional calcium hydroxide. These reported time shifts were estimated by determining the times in each case that were required to reach a given fixed value of heat flow, such as 0.002 W/g in Figure 9.

The final test of the calcium hydroxide addition consisted of evaluating its performance in the 50 % fly ash mixtures containing their requisite dosages of HRWRA. These calorimetric curves are presented in Figure 10. For both the Class C and Class F fly ashes with the requisite (mortar) dosage of HRWRA (that employed for the mortars described in Figures 1 and 2), a significant reduction in retardation is observed. For the Class C fly ash mixture, the hydration curve is nearly restored to the temporal location of the control paste with neither fly ash nor HRWRA, a reduction in retardation of about 5.5 h. Similarly, for the Class F fly ash mixture, a significant reduction of approximately 5 h in the retardation is achieved. These reductions in retardation produce similar reductions in setting times, as measured by needle penetration.[10] However. initial indications are that the calcium hydroxide may reduce compressive strengths, as the 28 d compressive strength of mortar cubes prepared with 5 % calcium hydroxide and the Class F fly ash was 84 % of that of the control Class F fly ash mortar with no calcium hydroxide.[7] A potential future research direction would be to evaluate other potential traditional sources of calcium ions, such as conventional accelerators including calcium nitrate and calcium chloride.[14]

Rapid Set Cement Additions in Detail

Further studies were conducted to examine how the reactions of the rapid set cement by itself are influenced by fly ash additions and the use of the HRWRA. Calorimetric results for these systems are presented in Figure 11. While the Class C ash and HRWRA each slightly retard the reactions of the rapid set cement and the Class F ash by itself actually accelerates them slightly, all hydration peaks occur within 1 h of the time observed for the control w/c=0.3 rapid set cement paste with neither fly ash nor HRWRA. This suggests that on an absolute time basis, the rapid set cement is less susceptible to excessive retardation than the Type II/V cement, for the mixtures examined in this study.

The performance of the rapid set cement, at an addition level of 10 %, was also evaluated in the Type II/V cement mixtures with 50 % fly ash and the requisite dosages of HRWRA, with the results being presented in Figure 12. In this case, there are two “separate” contributions of the rapid set cement, its own hydration reactions and its ability to accelerate the hydration of the ordinary portland cement/fly ash mixture. For the Class C ash mixture with its requisite dosage of HRWRA, the retardation is reduced by about 4 h and the hydration reactions of the rapid set cement are nearly immediate. For the Class F ash mixture, the retardation of the ordinary portland cement hydration is actually increased by about 8 h, while the rapid set cement hydration reactions peak at about 2 h after mixing. This implies that the Class F ash mixture would need to rely on the rapid set cement reactions for producing set and for supplying much of its 24 h strength. For this combination, the peak at 2 h is much greater than the heat liberated in the case of the Class C fly ash, implying a large interaction between the three powder materials. For this reason, the use of the rapid set cement with the cement/Class F fly ash/HRWRA combination examined in this study would require careful optimization and rigorous quality assurance for field use. Future research will focus on determining the contribution of this first hydration peak due to the rapid set cement to the overall setting behavior of the mixture. For example, rheological and set time measurements will be employed to better characterize the setting behavior of these systems.[10] Initial compressive strengths are generally positive, as a mortar prepared with 10 % of the rapid set cement, the Class C fly ash, and the 2 % gypsum addition exhibited a 28 d compressive strength that was 105 % of that of the equivalent mortar with no rapid set cement addition.[7] For the Class F fly ash, a 5 % addition of the rapid set cement produced a 28 d compressive strength that was 92 % of the reference Class F fly ash specimen, with equivalent strengths being produced at an age of 56 d.[7]

Conclusions

Isothermal calorimetry provides critical insights into the hydration/retardation behavior of HVFA paste mixtures. In this study, this technique has been successfully employed to identify two promising avenues for mitigating excessive retardation in HVFA mixtures:

additions of either a rapid set cement or calcium hydroxide powder. For the materials examined in this current study, both of these powder additions were effective in reducing measured retardation by up to 5 h. Further research will be required to evaluate the robustness of these mitigation strategies for other starting materials and for concretes produced under variable field conditions, and to investigate possible combinations of these two powder additions.

Acknowledgements

The author would like to thank the following companies for providing some of the materials employed in this study: Alcoa, GCC of America, Holcim, Lehigh Cement Corporation, OMYA, Separation Technologies, LLC, U.S. Concrete, and W.R. Grace & Co. -Conn. He would also like to thank Prof. Narayanan Neithalath of Clarkson University for providing materials and useful discussions, Mr. Max Peltz and Mr. John Winpigler of the Building and Fire Research Laboratory at NIST for their assistance with laboratory measurements, and Mr. Larry Roberts for a thorough review of the manuscript.

References

1. Mehta, P.K., "Global Concrete Industry Sustainability," *Concrete International*, V. 31, No. 2, 2009, pp. 45-48.

2. Mehta, P.K., "High-Performance High-Volume Fly Ash Concrete for Sustainable Development," *Proceedings of the International Workshop on Sustainable Development and Concrete Technology,* Beijing, China, 2004, pp. 3-14.

3. Wang, H., Qi, C., Farzam, H., and Turici, J., "Interaction of Materials Used in Concrete," *Concrete International*, V. 28, No. 4, 2006, pp. 47-52.

4. Roberts, L.R., and Taylor, P.C., "Understanding Cement-SCM-Admixture Interaction Issues," *Concrete International*, V. 29, No. 1, 2007, pp. 33-41.

5. ASTM C618-08a, “Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete,” ASTM International, West Conshohocken, PA, 2008, 3 pp.

6. ASTM C150-07, “Standard Specification for Portland Cement,” ASTM International, West Conshohocken, PA, 2007, 8 pp.

7. Bentz, D.P., Ferraris, C.F., De la Varga, I., Peltz, M.A., and Winpigler, J.A., “Mixture Proportioning Options for Improving High Volume Fly Ash Concretes,” in Proceedings of the International Conference on Sustainable Concrete Pavements: Practices, Challenges, and Directions, Federal Highway Administration, Sept. 15-17, Sacramento, CA, 2010.

8. Bentz, D.P., and Peltz, M.A., “Reducing Thermal and Autogenous Shrinkage Contributions to Early-Age Cracking,” *ACI Materials Journal*, V. 105, No. 4, 2008, pp. 414-420.

9. Bentz, D.P., “Blending Different Fineness Cements to Engineer the Properties of Cement-Based Materials,” accepted by *Magazine of Concrete Research*, 2010.

10. Bentz, D.P., and Ferraris, C.F., “Rheology and Setting of High Volume Fly Ash Mixtures,” *Cement and Concrete Composites*, V. 32, 2010, pp. 265-270.

11. Cost, V.T., and Gardiner, A., “Practical Concrete Mixture Evaluation via Semi-Adiabatic Calorimetry,” NRMCA Technology Forum, 2009, 21 pp.

12. Bentz, D.P., “Modeling the Influences of Limestone Filler on Cement Hydration Using CEMHYD3D,” *Cement and Concrete Composites*, V. 28, 2006, pp. 124-129.

13. Wei, X., Zhu, H., Li, G., Zhang, C., Xiao, L., “Properties of High Volume Fly Ash Concrete Compensated by Metakaolin or Silica Fume,” *Journal of Wuhan University of Technology-Materials Science Edition,* V. 22, No. 4, 2007, pp. 728-732.

14. Pacewska, B., Wilinska, I., Blonkowski, G., "Investigation of Cement Early Hydration in the Presence of Chemically Activated Fly Ash: Use of Calorimetry and Infrared Absorption Methods," *Journal of Thermal Analysis and Calorimetry*, V. 93, 2009, pp. 769-776.

Table 1. Oxide compositions of the Type II/V cement, the Class C and Class F fly ashes, the rapid set cement, and the cement kiln dust.

Component	**Type II/V cement (%)**	**Class C fly ash (%)**	**Class F fly ash (%)**	**Rapid set cement (%)**	**Cement kiln dust (%)**
SiO_2	21.1	38.38	59.73	15.40	14.46
Al_2O_3	4.5	18.72	30.18	13.74	4.81
Fe_2O_3	4.1	5.06	2.80	2.38	2.11
CaO	64.9	24.63	0.73	50.87	59.66
MgO	1.2	5.08	0.83	1.26	3.71
SO_3	2.5	1.37	0.02	12.52	11.89
Na_2O	0.31 equivalent	1.71	0.24	0.56 equivalent	0.73
K_2O	Not reported	0.56	2.42	Not reported	2.61
TiO_2	Not reported	1.48	1.60	Not reported	Not reported
P_2O_5	Not reported	1.24	0.08	Not reported	Not reported
Mn_2O_3	Not reported	0.02	0.02	Not reported	Not reported
SrO	Not reported	0.37	0.05	Not reported	Not reported
Cr_2O_3	Not reported	<0.01	0.03	Not reported	Not reported
ZnO	Not reported	<0.01	<0.01	Not reported	Not reported
BaO	Not reported	0.94	0.12		Not reported
Loss on ignition		0.26	0.79		Not reported

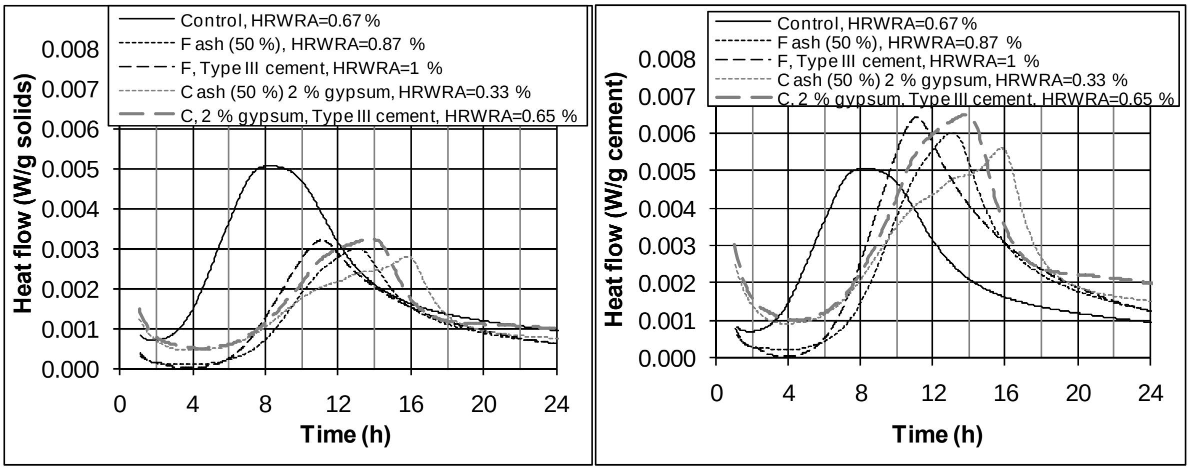

Fig. 1– Isothermal calorimetry curves for mortars (*w/cm* = 0.3) with and without 50 % fly ash replacement for cement normalized with respect to mass of solids (left) or with respect to mass of cement (right). HRWRA addition levels indicated in the legend are per unit mass of solids (cement + fly ash + gypsum). The type of cement (Type III vs. the control Type II/V) is a secondary variable as indicated in the legend; for heat flow, 1 W/g = 1548 BTU/(h·lb).

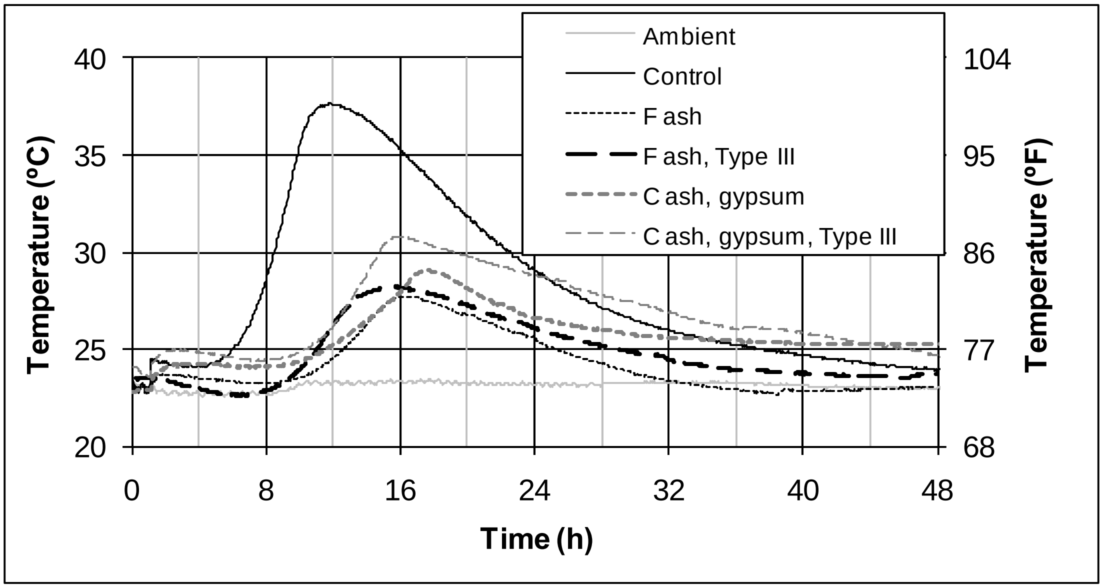

Fig. 2– Semi-adiabatic temperature rise curves for mortars (*w/cm* = 0.3) without (Control) and with 50 % fly ash replacement for cement. The type of cement (Type III vs. the control Type II/V) is a secondary variable as indicated in the legend.

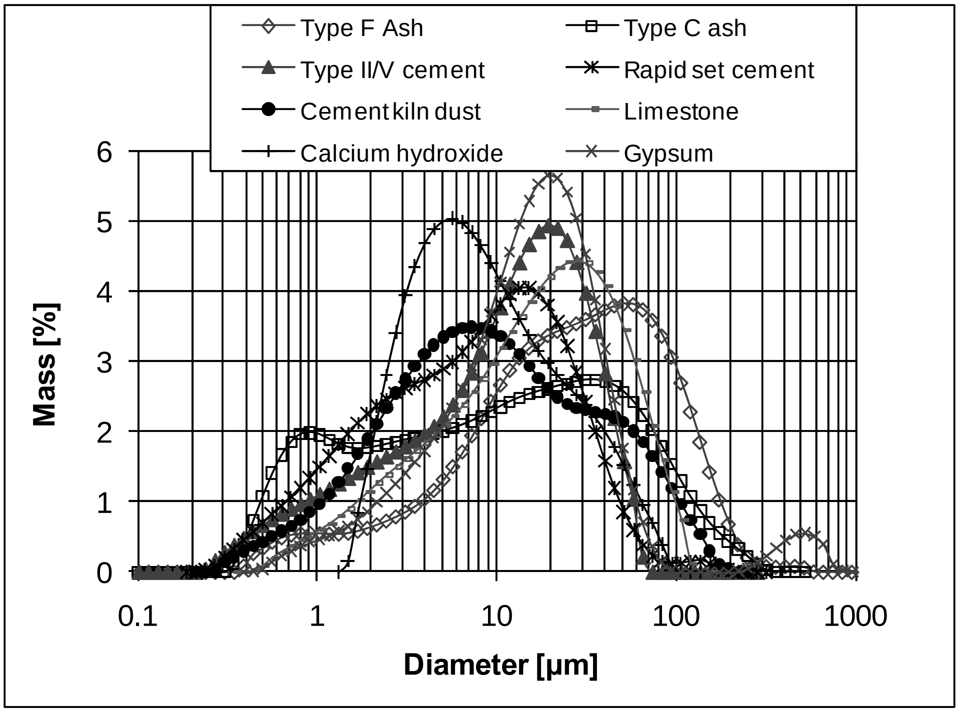

Fig. 3– Measured particle size distributions for the powders employed in the present study. The results are the average of six individual measurements and the error bars (one standard deviation) would fall within the size of the symbols. (One micrometer is equivalent to 3.9 x10^{-5} in.)

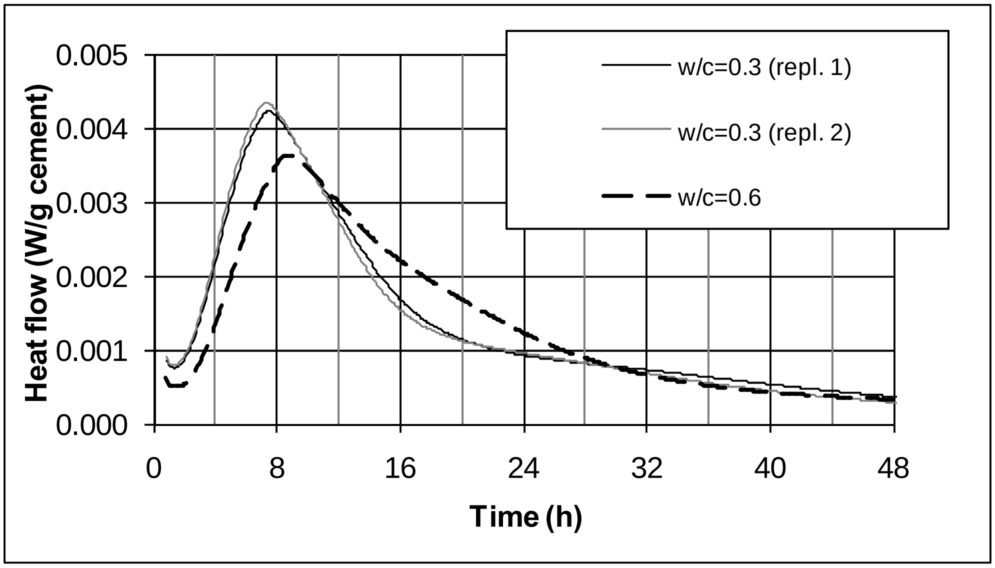

Fig. 4– Isothermal calorimetry curves for Type II/V cement pastes prepared at two different *w/c*. Results for two replicate specimens for the *w/c* = 0.3 cement paste are shown to provide an indication of typical variability; for heat flow, 1 W/g = 1548 BTU/(h·lb).

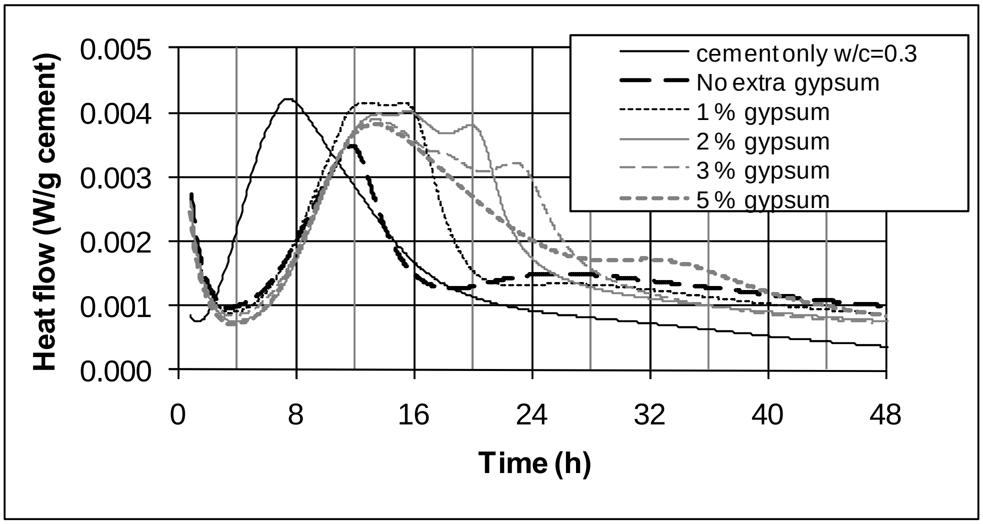

Fig. 5– Isothermal calorimetry curves for 50:50 Type II/V cement/Class C fly ash pastes prepared with various levels of calcium sulfate dihydrate additions; for heat flow, 1 W/g = 1548 BTU/(h·lb).

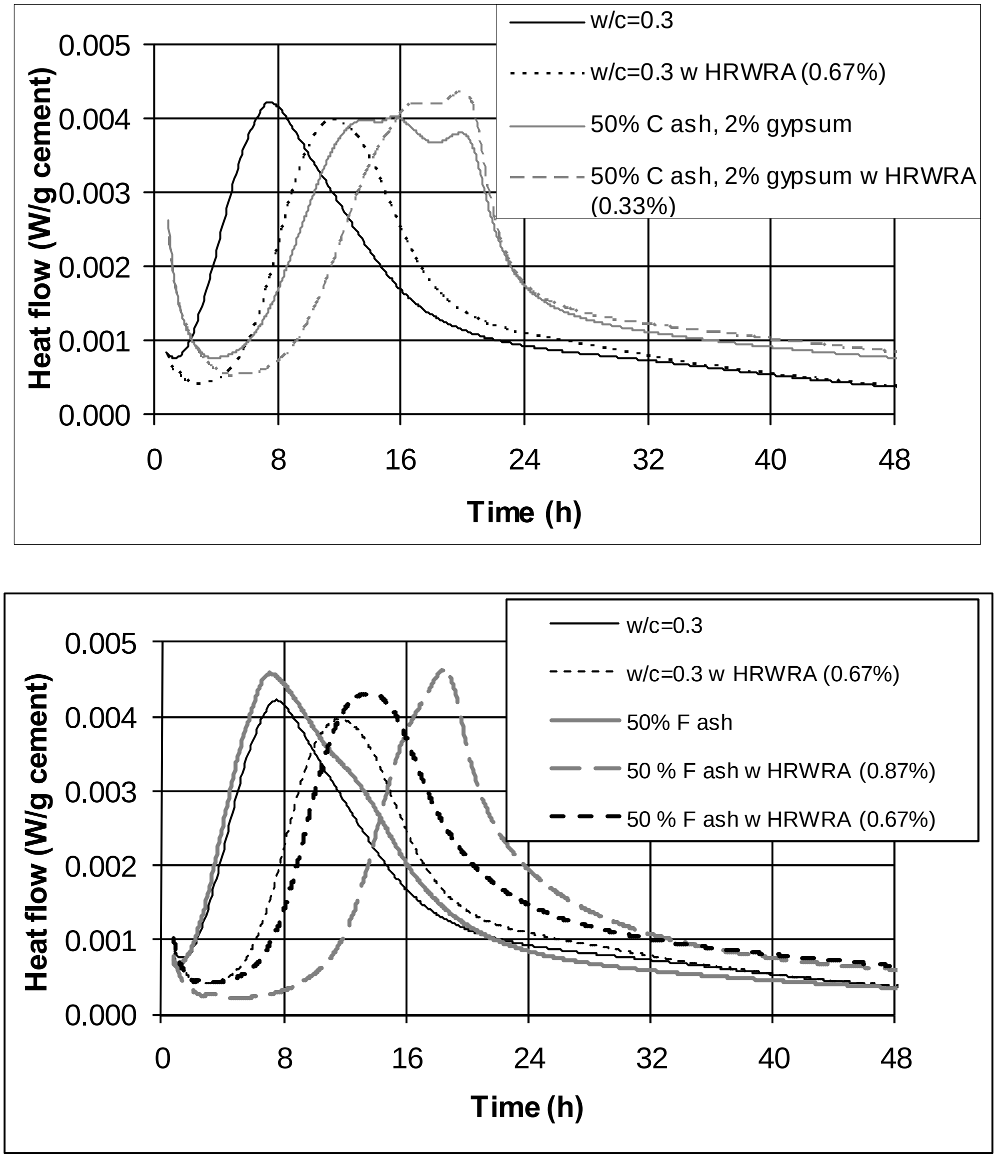

Fig. 6– Isothermal calorimetry curves for 50:50 Type II/V cement/fly ash pastes prepared with and without HRWRA for Class C (top) and Class F (bottom) ash. HRWRA addition levels indicated in the legend are per unit mass of cementitious material (cement + fly ash + gypsum); for heat flow, 1 W/g = 1548 BTU/(h·lb).

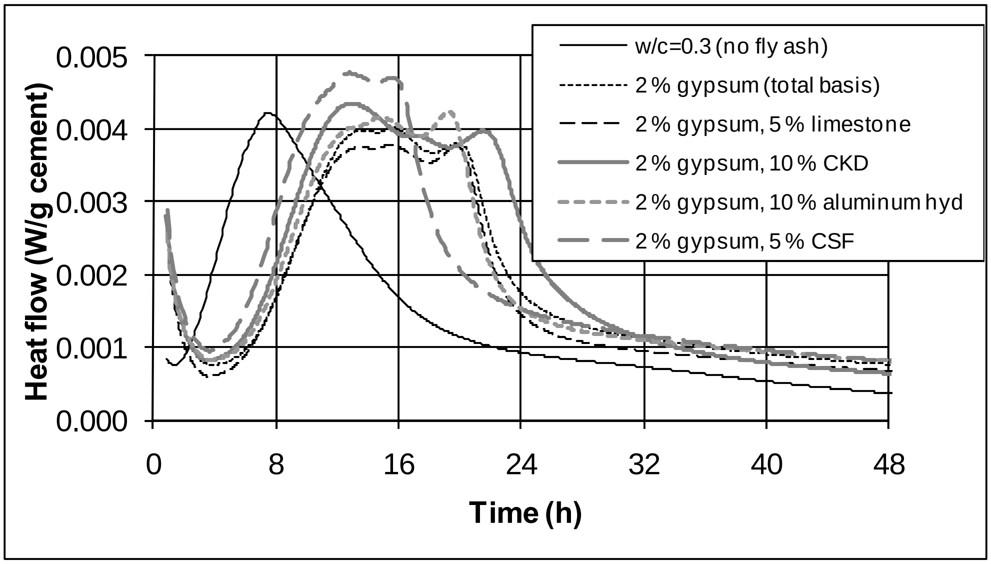

Fig. 7– Isothermal calorimetry curves for 50:50 Type II/V cement/Class C fly ash pastes prepared with various powder additions (all additional powder dosages by mass percent of total solids, but gypsum dosage is per unit mass cement + fly ash); for heat flow, 1 W/g = 1548 BTU/(h·lb).

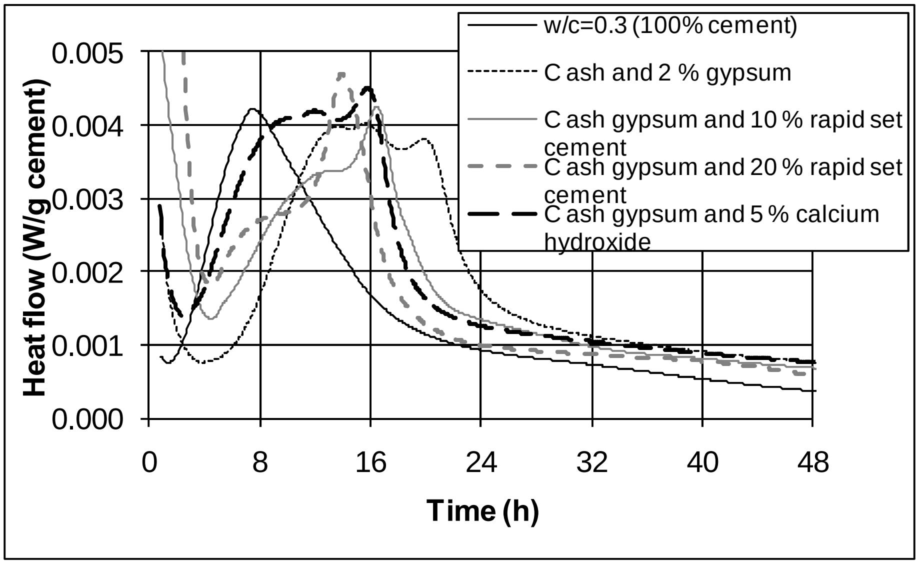

Fig. 8– Isothermal calorimetry curves for 50:50 Type II/V cement/Class C fly ash pastes prepared with calcium hydroxide or rapid set cement additions (all additional powder dosages by mass percent of total solids); for heat flow, 1 W/g = 1548 BTU/(h·lb).

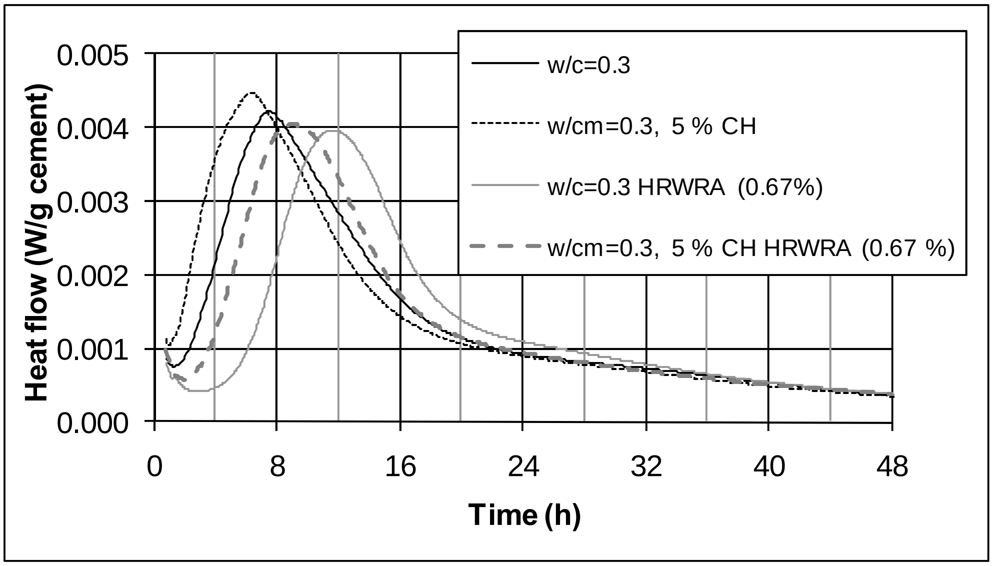

Fig. 9– Isothermal calorimetry curves for Type II/V cement pastes prepared with calcium hydroxide (CH in legend) and/or HRWRA additions (all dosages by mass percent of total solids); for heat flow, 1 W/g = 1548 BTU/(h·lb).

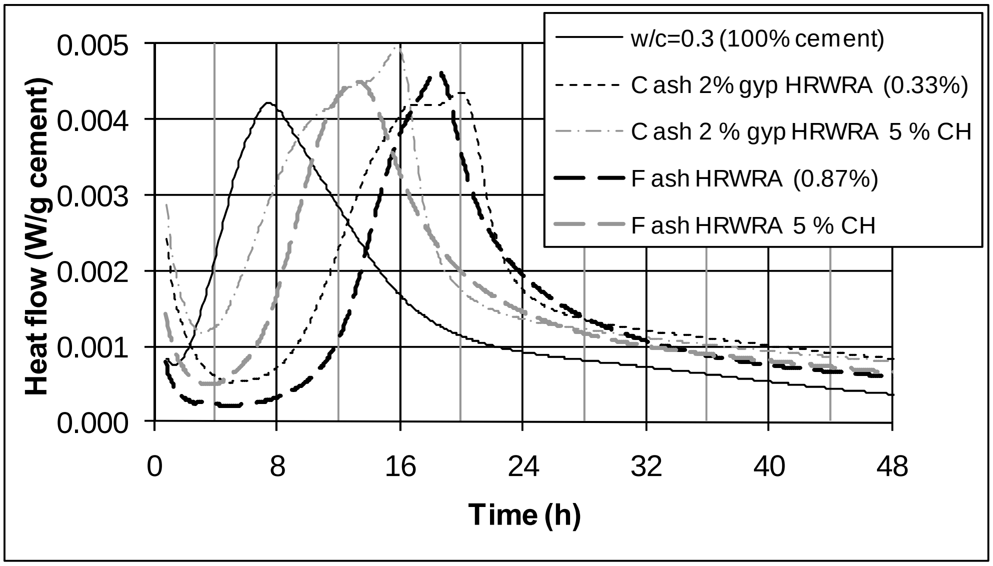

Fig. 10– Isothermal calorimetry curves for Type II/V cement/fly ash pastes prepared with and without 5 % calcium hydroxide (CH) additions (all dosages by mass percent of total solids); for heat flow, 1 W/g = 1548 BTU/(h·lb).

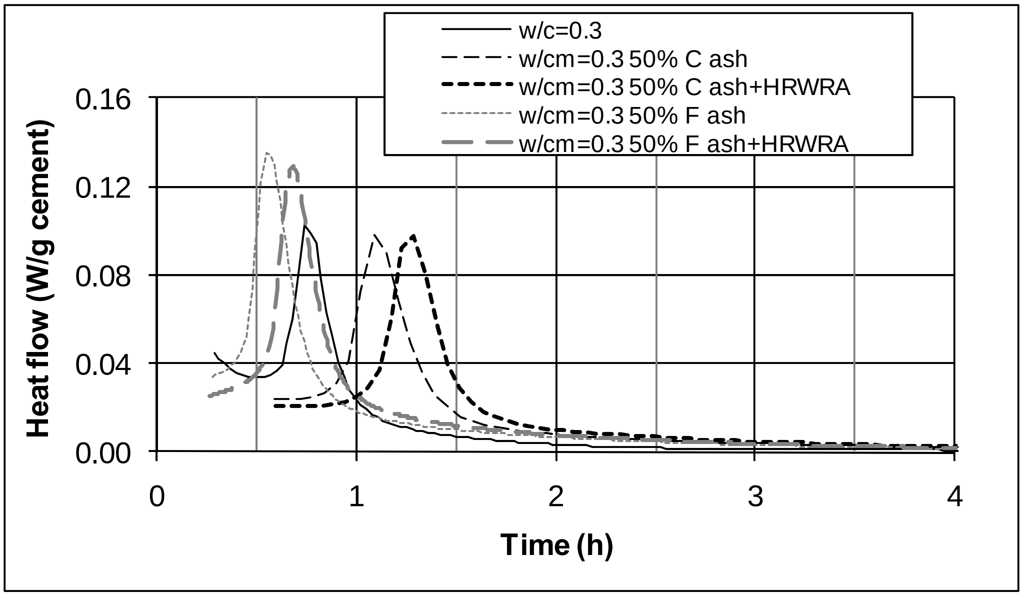

Fig. 11– Isothermal calorimetry curves for rapid set cement/fly ash pastes prepared with and without the HRWRA. HRWRA was added at a dosage of 0.33 % of total solids by mass; for heat flow, 1 W/g = 1548 BTU/(h·lb).

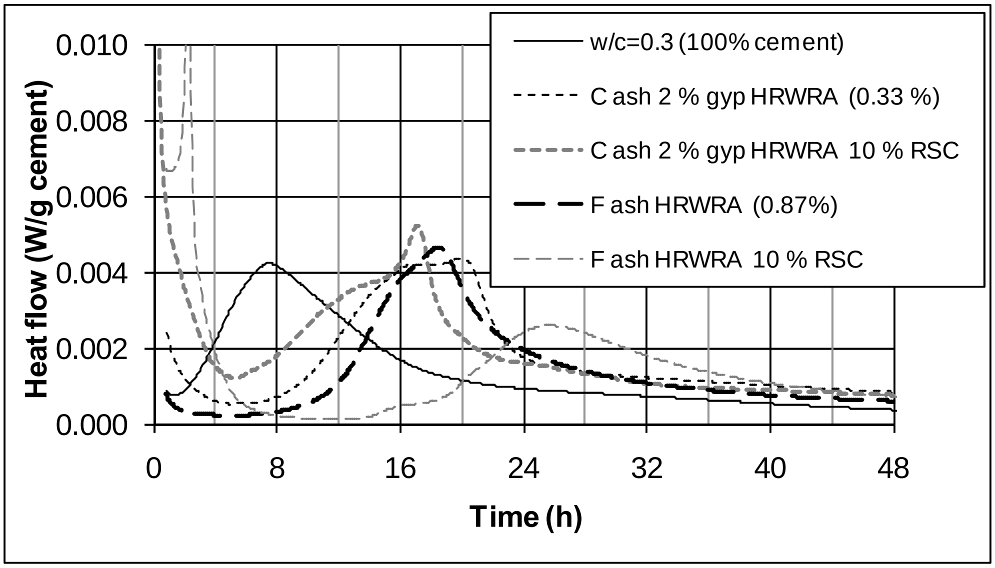

Fig. 12– Isothermal calorimetry curves for Type II/V cement/fly ash pastes prepared with and without the rapid set cement (RSC in legend); for heat flow, 1 W/g = 1548 BTU/(h·lb).