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Reducing Set Retardation in High Volume Fly Ash Mixtures with the Use of Limestone: Improving Constructability for Sustainability

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ABSTRACT

From a sustainability perspective, high volume fly ash (HVFA) concretes are attractive not only because of the reduction in cement content and its associated greenhouse gases that they provide, but also because they avoid landfilling excessive quantities of fly ash. These sustainability benefits are often tempered by practical constructability limitations that may exist for HVFA concretes: retardation and diminution of the early age reactions, delays in setting (and finishing operations), and lower early-age strengths. This paper explores the alleviation of these deficiencies in HVFA mixtures via the incorporation of fine limestone powders into ternary blends. Isothermal calorimetry and Vicat needle penetration measurements are employed to assess reaction rates and setting times, respectively. A systematic variation of the content and fineness of the limestone powder in mixtures containing either a Class C or a Class F fly ash indicates that setting times are linearly correlated with the surface area supplied by the limestone. Comparison of a limestone system to one containing an inert TiO_2 of similar particle size indicates that the acceleration and amplification effects of the limestone are due to both physical (nucleation) and chemical (additional calcium ions) processes. The results indicate that ternary blends with 40 % of the cement by volume replaced by 30 % to 35 % fly ash and 5 % to 10 % limestone at a constant water volume fraction can be achieved without significant delays in setting.

INTRODUCTION

The sustainability movement has renewed interest in reducing the cement content in concrete mixtures in an effort to reduce the carbon footprint of concrete manufacturing and to reduce production costs. One approach is to decrease the amount of portland cement in concrete by replacing a percentage of it with supplementary cementitious materials (SCMs). Fly ash, a byproduct of coal combustion, is a commonly used SCM, yet a large portion of it still ends up in landfills. By utilizing blended cements containing fly ash, not only can manufacturing costs be lowered, but landfill disposal can also be reduced.

Blended cement concretes that contain high volumes of fly ash (HVFA- typically 35 % to 60 % of the cement is replaced with fly ash) have shown attributes similar or superior to 100 % cement mixtures at late ages. However, these HVFA mixtures often exhibit retardation of reactions, low early-age strengths, and delayed setting times. Thus, the perceived potential sustainability of HVFA mixtures is often not realized since these mixtures are not implemented due to their lack of constructability [1]. These significant delays in setting are partially due to a dilution effect of having less of the reactive cement and are sometimes compounded by chemical incompatibilities between the fly ash and cement that retard or otherwise modify hydration behavior of the cement. Limestone powders have also been investigated for use as SCMs and have shown slightly increased early-age compressive strengths [2, 3] and accelerated hydration rates [2, 4]. Studies have indicated that finer particles generally yield shorter set times and accelerated hydration in blended cements [3, 5]. Kadri et al. [2] observed that additions of very finely ground silica fume, alumina or limestone increase the rate of hydration heat development and early-age compressive strength, but of these three, limestone had by far the greatest effect. Kadri et al. [2] and De Weerdt et al. [6] attributed this acceleration to both limestone's particle size (nucleation sites) and its chemical nature.

Other studies conducted to explore the behavior of cement – fly ash – limestone ternary blends compared to binary blends, show greater compressive strength and a partial alleviation of the negative effects observed in cement – fly ash mixtures [3, 6]. It has been further demonstrated that the beneficial effects of limestone additions observed in pure portland cement systems are amplified in the presence of fly ash [6, 7]. The objective of the current study is to determine whether limestone can reduce delays in setting. Further, this work will establish quantitative relationships between initial and final setting times of ternary mixtures and the total surface area provided by the limestone powder, for cement blended with either a Class C or a Class F fly ash.

MATERIALS AND EXPERIMENTAL METHODS

This study was conducted using Type I/II ordinary portland cement (OPC - ASTM C150 [8]). Two cements from the same manufacturer were obtained at different times and have slightly differing characteristics: the first was used with the Class C (ASTM C618-08a [9]) fly ash mixtures and the second with the Class F fly ash mixtures. Their respective Blaine fineness values are 367 m^2/kg and 383 m^2/kg, with estimated Bogue potential phase compositions of 52 % C_3S, 17 % C_2S, 8 % C_3A, and 10 % C_4AF for sample 1; and 51 % C_3S, 18 % C_2S, 7 % C_3A, and 11 % C_4AF by mass for sample 2, respectively. Both Class C and Class F fly ashes were considered because of their generally different behaviors when combined with OPC. The specific gravity and chemical composition of the OPCs and fly ashes are provided in Table 1. The Class C fly ash has a fairly high calcium oxide content of 24.63 % and is reactive with water. Both fly ashes have specific gravities that are lower than that of the OPCs, with the

Class F fly ash specific gravity being only about 70 % of the OPC value. While the Class C fly ash is of a size similar to that of the OPC, the Class F fly ash is significantly coarser, as exemplified by its higher d10, d50, and d90 (e.g., the diameter below which 90 % of the particles are found) values in Table 1. The Class C fly ash was specifically selected for this study based on its known incompatibilities and tendency to retard reactions [10].

Shown in Table 2 are the characteristics of the five limestone powders, four from the same manufacturer having median particle diameters of 17 μm, 3 μm, 1.4 μm, and 0.7 μm, and a nanoparticle-sized limestone obtained from a separate source. The median diameters of the micron-sized limestones are those reported by the manufacturer, while the size of the nano-limestone was obtained through microscopy techniques and reported to be in the range of 50 nm to 120 nm [11]. BET (Brunauer, Emmett, and Teller [12]) techniques using nitrogen adsorption were employed to obtain the surface area of each of the five limestones. Also in this study, a fine anatase (TiO_2), having a specific gravity of 3.9, a median diameter of 0.7 μm, and a BET surface area of 10.12 m^2/g was used as a chemically inert fine particle to examine if it could provide physical surfaces for the nucleation and growth of hydration products.

The cement pastes were designed to maintain constant volume fractions of water and powders, based on a control mixture with a water-to-cement ratio (*w/c*) of 0.35 by mass. Constant volumetric proportions were maintained to provide the fairest comparison of setting times. The nominal goal of the investigated mixtures was to replace 40 % of the cement by volume with other powders (fly ash or limestone). The design of each mixture and its corresponding *w/c* and water-to-cementitious material ratios (*w/cm*) by mass are provided in Table 3. Cement, fly ash, and limestone are all considered as cementitious materials in computing *w/cm.* Subsequently, any reference to a particular sample will refer to the ratio of its constituent materials. For example, a sample that contains volume percentages of 55 % cement powder, 40 % Class F fly ash and 5 % limestone with a 1.4 μm diameter will be referenced as "55-40F-5@1.4μm." The ratios chosen in this experiment were selected based on some preliminary lab work to investigate the optimal blends of OPC, fly ash, and limestone. No water reducing admixtures were used in this study, to avoid any confounding of their influence on hydration and setting with that of the powder materials. However, a recent study of cement/SCM/limestone ternary blends employing a high range water reducer has obtained results similar to those achieved in the present work [13].

Each mixture was individually prepared by first pre-blending the dry ingredients for 30 min in a powder blender, then mixing them with water in a high shear blender following the procedure developed by the Portland Cement Association [14]. After mixing, the paste was put into a truncated conical specimen for evaluation of setting times using the Vicat needle, and a small amount of the prepared material was placed in a glass vial for measurement of heat release using isothermal calorimetry.

The Vicat needle penetration tests were conducted according to the ASTM C191 standard [15], but with the following modifications. First, to minimize evaporation from the specimen surface during the course of the test, 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. The second modification was to redefine "final set" to be the time at which the Vicat needle penetrates no more than 1 mm into the paste. Some of the Vicat specimens exhibited excessive bleeding and although the needle would not

158 penetrate, it would continue to leave a mark on the surface for many hours as the bleed water
159 was slowly reabsorbed. In the ASTM C191 standard [15], the single laboratory precisions are
160 listed as 12 min (0.2 h) and 20 min (0.33 h) for the initial and final times of setting, respectively.
161 All set time measurements were conducted inside a walk-in environmental chamber maintained
162 at (25.0 ± 1.0) ˚C.
163 Following the general guidelines provided in the ASTM C1702 standard [16], isothermal
164 calorimetry was conducted for a period of at least 24 h, using paste specimens having a mass of
165 between 4.98 g and 5.26 g. The prepared paste was carefully placed in the glass calorimeter
166 specimen vials, the vials were sealed, and the sealed vials were then loaded into the calorimeter
167 along with a reference vial containing only dry cement powder. Using this procedure, the initial
168 "mixing" peak that occurs when water contacts cement was not examined in this study. For this
169 technique, the average absolute difference between replicate specimens of cement paste was
170 measured to be 3.16×10^{-5} W/g (cement), with a maximum absolute difference of 9.10×10^{-5} W/g
171 (cement), for measurements conducted between 1 h and 24 h after mixing. Calorimetry data was
172 collected as a quantitative indication of the ongoing reactions and because of its high correlation
173 with the stiffness and compressive strength of mortars and pastes [3, 17].
174
175 **RESULTS AND DISCUSSIONS**
176 Vicat needle penetration and isothermal calorimetry data for all mixtures are presented and
177 compared in the following figures and tables. Calorimetry data provides a comparison of the
178 ongoing reaction rates (acceleration/retardation/amplification/diminution of the heat flow
179 compared to the 100 % cement paste), while Vicat needle penetration depends on chemical
180 reaction rates along with the accompanying physical process of building "bridges" between the
181 cement particles to induce setting.
182
183 **Vicat Results**
184 Figure 1 and Table 4 show the results of the Vicat needle penetration tests for both classes of fly
185 ash. By definition, the time of a 25 mm penetration of the Vicat needle is the initial set time, as
186 indicated in each plot by a horizontal dashed line. For the Class C fly ashes, the mixtures
187 with 5 % limestone are shown in lighter shades and marked with a triangle, while those
188 with 10 % limestone are in darker shades and marked with a square.
189 The 60-40 fly ash mixtures containing no limestone exhibit the greatest delays in initial
190 and final set times due to dilution (Class F and Class C) and retardation (Class C) effects. The
191 lack of retardation in the chemical reactions due to the Class F fly ash is verified by examining
192 the heat flow curves in Figure 2. The initial set times of these mixtures are delayed from those of
193 their corresponding control by 3.66 h for the C ash and 0.85 h for the F ash. It is clearly evident
194 that for both fly ashes examined in this study, an increase in volumetric percentage and/or a
195 decrease in particle size of limestone reduce the setting times, systematically approaching that of
196 the control (100 % cement) mixture. Mounanga et al. [3] have similarly observed set
197 acceleration in ternary mixtures containing fly ash and limestone, noting that the acceleration
198 was more pronounced with higher limestone contents. Figure 1 indicates that even at a low 5 %
199 volume fraction, introduction of limestone has an accelerating effect on these ternary blends, but
200 perhaps more important than the amount of limestone is its particle size. Each progressive
201 decrease in limestone particle size provides a further decrease in set times, but for the Class C fly
202 ash mixtures and the limestones examined in this study, a 5 % replacement by volume is not
203 sufficient to reach the set time of the control. Doubling the amount of limestone significantly
204 reduces the set time for all sizes of limestone (in the Class C fly ash mixtures), but the best match

to the original set time of the control 100 % cement paste is provided by the mixture with 10 % nano-limestone. For the Class F fly ash mixtures, the 5 % nano-limestone more than adequately mitigates the delays in set times caused by the 40 % replacement of cement; for this ash, perhaps a limestone with a diameter between 0.7 μm and 0.12 μm or a smaller amount of the nano-limestone could be used.

Calorimetry Results

Showing the heat flow per gram of cement and the cumulative heat release per milliliter of water for each mixture, Figure 2 uses the same line and marker styles as the Vicat results in Figure 1. In each plot in Figure 2, the vertical cross marks indicate the initial Vicat set times. The heat flow plots are scaled per gram of cement to provide an indication of the relative reactivity of the cement in each mixture, assuming that the fly ashes and limestones are nominally inert during the first hours of hydration. The cumulative heat release is normalized per volume of water in each mixture to examine the relationship between heat generation and the filling of this pore (water) volume with hydration products [17].

Type I/II cements typically exhibit a heat flow curve that has two (partially overlapping) peaks, generally occurring within the first 24 h. The first peak represents reaction of the calcium silicates, while the second peak (or shoulder in some cases) is generally related to a renewed period of aluminate reactivity. The effect of a 40 % fly ash replacement on the heat flow curve is distinct for the representatives of each class of fly ash employed in the current study. The Class C fly ash introduces a sharp amplification of the second peak, and both peaks are greatly retarded from those of the control mixture (e.g., by more than 3 h). Conversely the Class F fly ash has a negligible effect on heat flow and functions mainly as a diluent at early ages.

Introducing limestone into the cement-fly ash mixtures does not greatly affect the basic (two-peak) shape of the heat flow curves, but it does both accelerate and amplify the heat flow, as observed in previous studies [3, 17]. The observed degree of acceleration and amplification is greater as the particle size of the limestone decreases, or as the total limestone particle surface area increases. Cumulative heat data was also collected for the first 24 h after preparing the mixtures (Table 4), although only the first 10 h is shown in Figure 2. As with the Vicat results, for the Class C fly ash, the 60-30C-10@nano mixture best reflects the heat of the control mixture through the first 9 h, but it then drops below the control curve. At an age of 24 h, this nano-limestone mixture only has 77 % of the cumulative heat release per milliliter of water of the pure cement mixture; still, it offers the most improvement in 1 d cumulative heat release and therefore likely in 1 d strength, as has been observed in mortars in a previous study [17]. It is also notable that all of the mixtures for a given fly ash and a given limestone replacement level have similar cumulative heat release values at their respective times of initial set.

Discussion of Findings

Owing to differences in composition, each mixture behaved differently during mixing and setting. There were some samples that exhibited substantial bleeding; this was most apparent in the mixtures containing the Class F fly ash, likely due to its lower specific gravity and larger particle size, an effect that was mitigated with the addition of the finer limestones. While the mixtures were all designed to have the same volume fraction of water, as they were composed of various quantities of several materials, they still differed in their observable rheology. Visually, this correlated to component particle size (as the coarser limestones and fly ashes were less viscous than their finer counterparts) or equivalently to total particle surface area. The high viscosities could be reduced through the addition of water reducers, but water reducers were not

included in the present study to avoid their confounding influences on hydration and setting. While the viscosity (and yield stress) varied from one mixture to another, preparing the Vicat and isothermal calorimetry specimens was readily achievable in every case.

Apparent when comparing the results portrayed in Figures 1 and 2, the Vicat tests and calorimetry data support each other well. The mixtures that best matched the controls in the Vicat penetration test results in Figure 1 were also the most similar to the 100 % OPC control in cumulative heat release in Figure 2. For each fly ash at each limestone volume fraction, the cumulative heat release at initial set was approximately a constant value. Since these mixtures were all formulated with the same volume fraction of water, one can hypothesize that each would require a similar volume of hydration product formation to bridge the cement particles and produce setting. At the same volume fraction of limestone (5 %), the Class C fly ash mixtures required a greater amount of heat to produce initial setting than the Class F fly ash mixtures. This is likely due to the additional initial heat provided by the Class C fly ash reacting during the first few hours, as seen at the far left of the heat flow curves in Figure 2. This particular Class C fly ash is hydraulic and will flash set when mixed alone with water [17]. In a blended system, these fly ash reactions contribute heat but apparently don't contribute substantially to building the necessary bridges between the (flocculated) cement particles. For each fly ash, these heat release values at initial set are substantially higher than those of the control system, as the addition of fly ash and/or limestone particles dilutes and further separates the remaining cement particles (higher *w/c* in Table 3); naturally, more hydration and its accompanying heat release would be necessary to achieve setting in this case, similar to an increase in *w/c* having minimal effects on calorimetry but causing noticeable set time delays [18].

The 60-35-5@anatase mixtures were useful in distinguishing the cause of the acceleration and amplification seen in the mixtures containing the same volumetric proportions of limestone, particularly as the anatase has the same median particle diameter as the 0.7 μm limestone. For both classes of fly ash, the anatase mixture shows a slight acceleration from the 60-40 mixture in heat flow, but less so for the Vicat results. This small acceleration may be attributed partially to the decrease in fly ash concentration that accompanies the addition of the anatase. The other contribution to this acceleration may be the increased surface area and number of nucleation sites provided by the finer anatase particles. The anatase mixtures also exhibited higher viscosities, as would be expected with fine anatase particles replacing coarser fly ash ones. In comparison, the acceleration/amplification provided by the 1.4 μm limestone is dramatically larger (see also the 24 h heat release values in Table 4), supporting that the limestone plays both physical and chemical roles in influencing the cement and fly ash reactions at early ages [2, 17]. While $CaCO_3$ (limestone) is not very soluble at the higher pHs typical of pore solutions, the initial contact of the (three) powders is with a fairly neutral pH distilled water [17]. Finer limestone powders would be expected to dissolve more rapidly during this initial contact, prior to the pH of the pore solution increasing to over 12 due to concurrent cement (and fly ash) dissolution. In support of this hypothesis, preliminary measurements of calcium ion concentrations in centrifuged pore solutions have indeed indicated a higher calcium concentration for a cement-fly ash paste with a nano-limestone addition vs. one without limestone.

The ternary mixture containing Class C fly ash that best reflects the control is the 60-30C-10@nano mixture; it had an initial set time delay of only 9 min (0.15 h). The best mixture containing the Class F fly ash would be somewhere between the 0.7 μm and 0.12 μm (nano) limestone mixtures. An optimal mixture can be achieved by using a limestone with a median diameter between those two values, or perhaps by slightly reducing the amount of limestone in

the nano mixture. It is also evident from the data shown in Figure 1 that decreasing particle size from 0.7 μm to 0.12 μm (nano) has a greater accelerating effect than any other decrement (e.g., with the F ash, decreasing from 17 μm to 3 μm and even 1.4 μm had very little effect on the initial set time and hydration heat curves). Although throughout this paper, the limestones have been referred to by their median particle diameters, it is likely that their surface area better constitutes the extent of their acceleration and amplification of hydration. An additional variable that could influence this acceleration and amplification is the crystallinity of the limestone; this parameter was not assessed in the present study, but could be a topic for future research.

Figure 3 explores the relationship between total limestone surface area per unit volume of paste and set times. The limestone surface area was calculated based on the mixture proportions and the measured BET value for each limestone powder (Table 2). For each individual fly ash at each limestone concentration, a linear relationship with a high correlation coefficient (R^2) is observed for both initial and final set times. Linear relationships with a positive slope and $R^2 \geq 0.92$ (not shown) between cumulative heat release at a specific early age (4 h or 8 h for example) and surface area provided by the limestone were also observed. Unfortunately, whether limestone is providing acceleration and amplification due to its dissolution (chemical) or due to providing nucleation sites and additional surface area for the growth of hydration products (physical), a linear relationship between surface area and set times (or heat release) would be expected. The fact that the data points for anatase included in Figure 3 lie significantly above the limestone lines in both cases further supports the hypothesis that at least part of the acceleration and amplification produced by the limestone is due to chemical effects.

While the plots in Figure 3 do not clearly delineate between the specific mechanisms of fine limestone powder acceleration, they do provide a useful tool for estimating the limestone surface area that must be provided to each system to mitigate the delayed setting response of a high volume fly ash mixture. The procedure to estimate the necessary limestone particle size (distribution) for a given set of mixture proportions would be straightforward based on the individual lines in Figure 3. To estimate the limestone volume fraction necessary given a specific limestone particle size distribution (surface area), one would need to interpolate between or extrapolate beyond the lines established for specific volume fractions, as exemplified by the two lines for the Class C fly ash in Figure 3. To demonstrate this more clearly, for the Class C fly ash mixtures, the initial set time results are plotted against limestone volume fraction in Figure 4. For a given limestone, the lines in Figure 4 could be used to estimate the required limestone replacement level to provide equivalence (or any desired delay) in initial set time relative to that of the control mixture. Thus, a standardized procedure could be to 1) determine the set time for a control mixture or that desired for the HVFA mixture, 2) determine the current set time for the HVFA mixture, 3) determine the set time for one level of limestone replacement (say 5 %), 4) estimate the required limestone replacement level to achieve the desired set time using a law of mixtures, and 5) prepare a trial batch with this calculated limestone replacement level to verify performance. The law of mixtures would simply provide a linear-based estimate of the required limestone replacement level as:

$$\%\ limestone\ for\ desired\ performance = \left[\frac{t_{HFVA} - t_{desired}}{t_{HVFA} - t_{limestone}}\right] * (\%\ limestone\ in\ test\ mixture) \qquad (1)$$

where t_{HVFA} is the set time of the HVFA mixture with no limestone replacement, $t_{desired}$ is the desired set time (e.g., that of the control 100 % OPC mixture), and $t_{limestone}$ is the measured set

time of the mixture with the test level of limestone replacement. This procedure could be employed for engineering either the initial or the final set times of the ternary blend mixture.

CONCLUSIONS

Based on the materials examined in this study, the following conclusions can be drawn:

1) fine (on the order of 1 μm median diameter) limestone powder replacement for a portion of the fly ash in a high volume fly ash mixture is an effective approach to mitigating excessive delays in setting times,

2) the performance of the limestone in this respect is related to its surface area (as measured using BET methods),

3) a linear relationship exists between the initial and final set times and the surface area provided by the limestone replacements in each type of ternary mixture,

4) for a fixed water volume fraction, the cumulative heat release per milliliter of water at initial set is constant for a given fly ash with a given concentration of limestone replacement, and

5) each cement/fly ash combination will likely exhibit a unique early-age behavior with some requiring relatively large additions (10 % or more) of a very fine limestone and others needing only a minor addition of a coarser limestone powder to adequately mitigate setting time delays.

This study has focused on the alleviation of delayed setting times via the addition of fine limestone powders to HVFA paste mixtures. Other properties such as compressive strength development and autogenous shrinkage at early ages (since the limestone powders being employed are quite fine) should be evaluated in the future to establish their relationship to the characteristics of the limestone powders in mortar/concrete mixtures. The results to date indicate a promising potential for these ternary mixtures to achieve equivalent performance to 100 % OPC systems, with substantial cost, energy, and CO_2 footprint reductions, successfully achieving the joint critical objectives of constructability and sustainability.

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REFERENCES

1) Cost, V.T. Concrete Sustainability Versus Constructability – Closing the Gap, 2011 International Concrete Sustainability Conference, Boston, 2011.
2) Kadri E.H., S. Aggoun, G. De Schutter, and K. Ezziane. Combined Effect of Chemical Nature and Fineness of Mineral Powders on Portland Cement Hydration. *Materials and Structures*, Vol. 43, No. 5, 2009, pp. 665-673**.**
3) Mounanga P., M.I.A. Khokhar, R. El Hachem, and A. Loukili. Improvement of the Early-Age Reactivity of Fly Ash and Blast Furnace Slag Cementitious Systems Using Limestone Filler. *Materials and Structures*, Vol. 44, 2011, pp. 437-453.
4) Menendez G., V. Bonavetti, and E.F. Irassar. Strength Development of Ternary Blended Cement with Limestone Filler and Blast-Furnace Slag. *Cement and Concrete Composites*, Vol. 25, No. 1, 2003, pp. 61-67

5) Quian J., C. Shi, and Z. Wang. Activation of Blended Cements Containing Fly Ash. *Cement and Concrete Research*, Vol. 31, No. 8, 2001, pp.1121-1127.
6) De Weerdt K., M. Ben Haha, G. Le Saout, K.O. Kjellsen, H. Justnes, and B. Lothenbach. Hydration Mechanisms of Ternary Portland Cements Containing Limestone Powder and Fly Ash. *Cement and Concrete Research*, Vol. 41, 2011, pp. 279-291.
7) De Weerdt K., K.O. Kjellsen, E. Sellevold, and H. Justnes. Synergy Between Fly Ash and Limestone Powder in Ternary Cements. *Cement and Concrete Composites*, Vol. 33, No. 1, 2010, pp. 30-38.
8) ASTM C150. Standard Specification for Portland Cement; 2009.
9) ASTM C618-08a. Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. 2008
10) Bentz D.P., C.F. Ferraris, I. De la Varga, M.A. Peltz, and J. Winpigler. Mixture Proportioning Options for Improving High Volume Fly Ash Concretes. *International Journal of Pavement Research and Technology*, Vol. 3, No. 5, 2010, pp. 234-240.
11) Sato T., and J. Beaudoin. Effect of Nano-$CaCO_3$ on Hydration of Cement Containing Supplementary Cementitious Materials. *Advances in Cement Research*, Vol. 23, No. 1, 2011, pp. 1-11.
12) Brunauer, S., P.H. Emmett, and E. Teller. Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*, Vol. 60, 1938, 309-319.
13) Cost, T. Optimization of Concrete Paving Mixtures for Sustainability and Performance. Submitted to the International Conference on Concrete Pavements, 2012.
14) Helmuth R.A., L.M. Hills, D.A. Whiting, and S. Bhattacharja. Abnormal Concrete Performance in the Presence of Admixtures. 1995 PCA serial # 2006.
15) ASTM C191-08. Standard Test methods for Time of Setting of Hydraulic Cement by Vicat Needle. 2008.
16) ASTM C1702-09a. Standard Test Method for Measurement of Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry. 2009.
17) Bentz D.P., T. Sato, I. De la Varga, and J. Weiss. Fine Limestone Additions to Regulate Setting in High Volume Fly Ash Mixtures. *Cement and Concrete Composites*, Vol. 34, No. 1, 2012, pp. 11-17.
18) Bentz, D.P., M.A. Peltz, and J. Winpigler. Early-Age Properties of Cement-Based Materials: II. Influence of Water-to-Cement Ratio. *ASCE Journal of Materials in Civil Engineering*, Vol. 21, No. 9, 2009, pp. 512-517.

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451 **TABLE 1 Oxide Composition Percent by Mass and Physical Characteristics of the Cement**
452 **and Fly Ashes**

	Cement Sample 1 ASTM C150 I/II	Class C Fly Ash	Cement Sample 2 ASTM C150 I/II	Class F Fly Ash
SiO_2	19.51	38.38	19.40	59.73
Al_2O_3	4.86	18.72	4.86	30.18
Fe_2O_3	3.15	5.06	3.62	2.80
CaO	61.76	24.63	61.22	0.73
MgO	3.61	5.08	4.22	0.83
SO_3	3.12	1.37	3.11	0.02
CO_2	0.95	-	1.71	-
Alkalies (equivalent)	0.48	-	0.45	-
Insoluble Residue	0.18	-	0.11	-
Na_2O	-	1.71	-	0.24
K_2O	-	0.56	-	2.42
Loss on ignition	2.33	0.26	2.55	0.79
Specific gravity	3.15	2.63	3.15	2.16
d (10 %)	1.36 μm	0.85 μm	1.73 μm	3.23 μm
d (50 %)	11.49 μm	10.30 μm	11.83 μm	25.34 μm
d (90 %)	32.67 μm	69.37 μm	35.50 μm	99.06 μm

453
454

455 **TABLE 2 Calcium and Magnesium Carbonate Contents, Median Diameters, Specific**
456 **Gravities and Measured Surface Areas of the Five Limestones Investigated**

	17 µm	**3 µm**	**1.4 µm**	**0.7 µm**	**nano**
$CaCO_3$	95	96	98	98	> 98
$MgCO_3$	2	2	1	1	negligible
Median diameter (µm)	17	3	1.4	0.7	0.05 to 0.12
Specific gravity	2.71	2.71	2.70	2.70	2.70
BET surface area (m^2/g)	0.831	2.42	7.06 (0.14)[A]	9.93	19.4

457 [A]Standard deviation amongst three replicate specimens for this limestone.
458
459

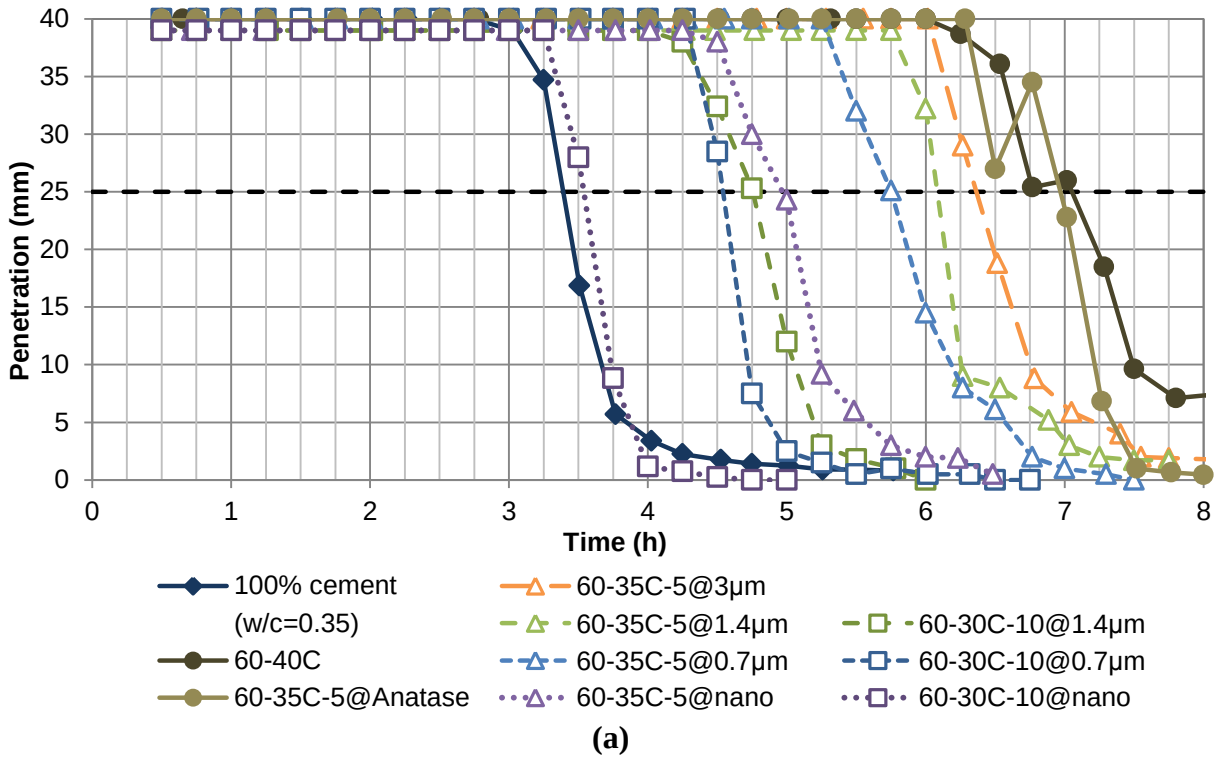
TABLE 3 Percentages by Volume of Cement, Fly Ash and Limestone for Each Mixture and their Respective *w/c* and *w/cm*

Cement	Fly Ash	Limestone		*w/c*	*w/cm*
		%	Size		
Ternary Mixtures with Class C Fly Ash					
100	-	-	-	0.350	0.350
60	40	-	-	0.583	0.375
60	35	(5 % TiO_2)		0.583	0.367
60	35	5	3.0 μm	0.583	0.374
60	35	5	1.4 μm	0.583	0.374
60	35	5	0.7 μm	0.583	0.374
60	35	5	nano	0.583	0.374
60	30	10	1.4 μm	0.583	0.374
60	30	10	0.7 μm	0.583	0.374
60	30	10	nano	0.583	0.374
Ternary Mixtures with Class F Fly Ash					
100	-	-	-	0.350	0.350
60	40	-	-	0.583	0.400
60	35	(5 % TiO_2)		0.583	0.388
60	35	5	17 μm	0.583	0.396
60	35	5	3.0 μm	0.583	0.396
60	35	5	1.4 μm	0.583	0.396
60	35	5	0.7 μm	0.583	0.396
60	35	5	nano	0.583	0.396

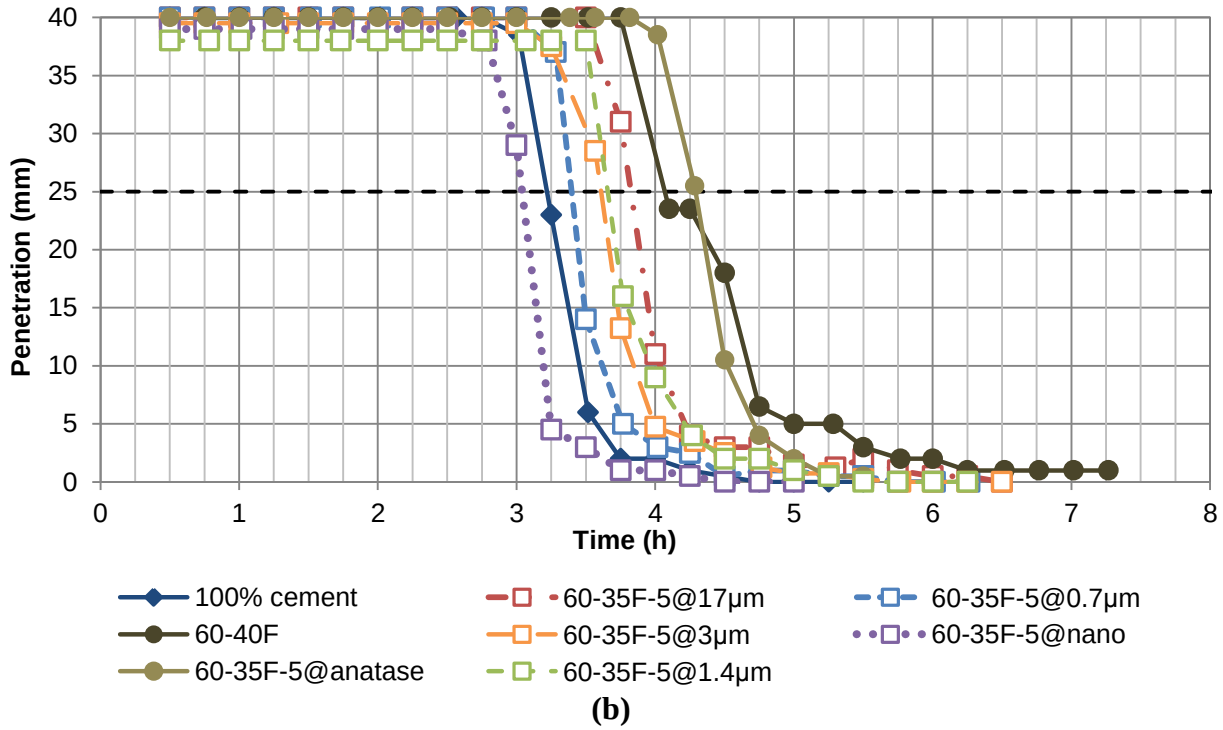
464 **TABLE 4 Set Times and Cumulative Heat per Milliliter of Water at the Initial Set, Final**
465 **Set and 24 Hours for Each Mixture**

Class C Fly Ash							
	Initial Set Time (h)	Delay from control (h)	Final Set Time[B] (h)	Delay from control (h)	Cumulative Heat (J/mL water) at initial set	at final set	at 24 h
100-0-0	3.39	-	5.26	-	36.0	100.2	570.2
60-40C-0	7.05	3.66	> 8.76	> 3.50	54.1	> 91.3	384.5
60-35C-5@anatase	6.97	3.58	7.52	2.26	52.3	63.5	394.8
60-35C-5@3.0 μm	6.36	2.97	8.02	2.76	50.2	85.7	390.0
60-35C-5@1.4 μm	6.08	2.69	7.75	2.49	55.2	96.8	407.5
60-35C-5@0.7 μm	5.75	2.36	7.00	1.74	55.4	87.6	415.4
60-35C-5@nano	4.97	1.58	6.48	1.23	57.7	97.9	419.7
60-30C-10@1.4 μm	4.76	1.36	5.78	0.52	45.5	72.3	429.5
60-30C-10@0.7 μm	4.57	1.18	5.50	0.24	43.5	68.0	434.7
60-30C-10@nano	3.54	0.15	4.25	-1.01	44.2	65.1	440.1
Class F Fly Ash							
	Initial Set Time (h)	Delay from control (h)	Final Set Time[B] (h)	Delay from control (h)	Cumulative Heat (J/mL water) at initial set	at final set	at 24 h
100-0-0	3.22	-	4.25	-	30.7	70.6	636.7
60-40F-0	4.07	0.85	6.25	2.00	39.5	107.9	421.8
60-35F-5@anatase	4.29	1.07	5.25	1.00	37.5	65.7	445.9
60-35F-5@17 μm	3.83	0.61	5.75	1.50	43.5	106.3	427.3
60-35F-5@3.0 μm	3.57	0.35	4.88	0.63	40.2	81.1	433.3
60-35F-5@1.4 μm	3.66	0.44	5.00	0.75	46.6	93.7	449.7
60-35F-5@0.7 μm	3.40	0.18	4.50	0.25	43.3	82.6	453.8
60-35F-5@nano	3.04	-0.18	3.75	-0.50	45.1	70.3	461.1

466 [B] In this study, "final set" is defined as the time when the penetration of the Vicat needle is less
467 than or equal to 1 mm.
468



(a)



(b)

FIGURE 1 Vicat results for a) Class C and b) Class F fly ash ternary mixtures.

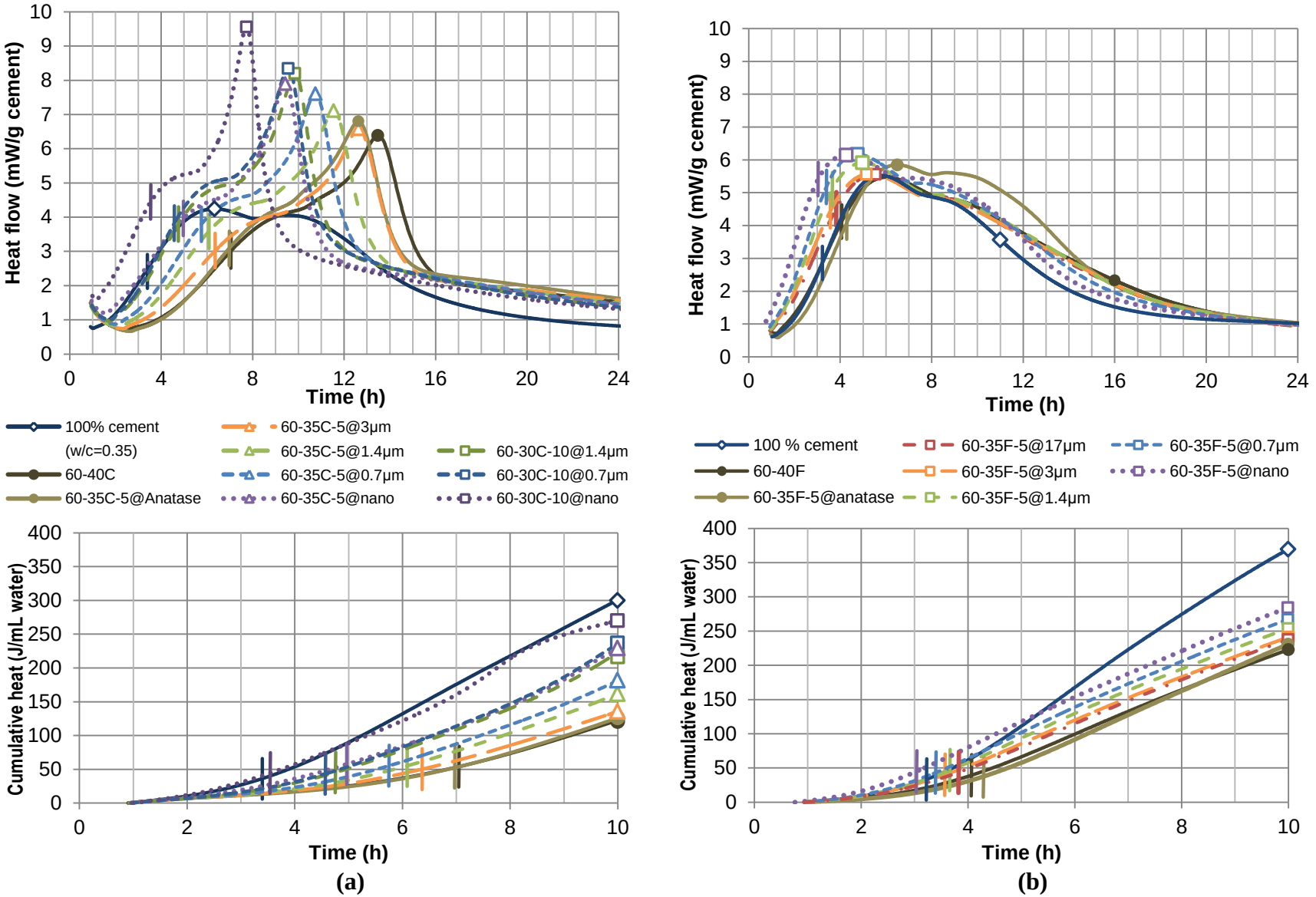
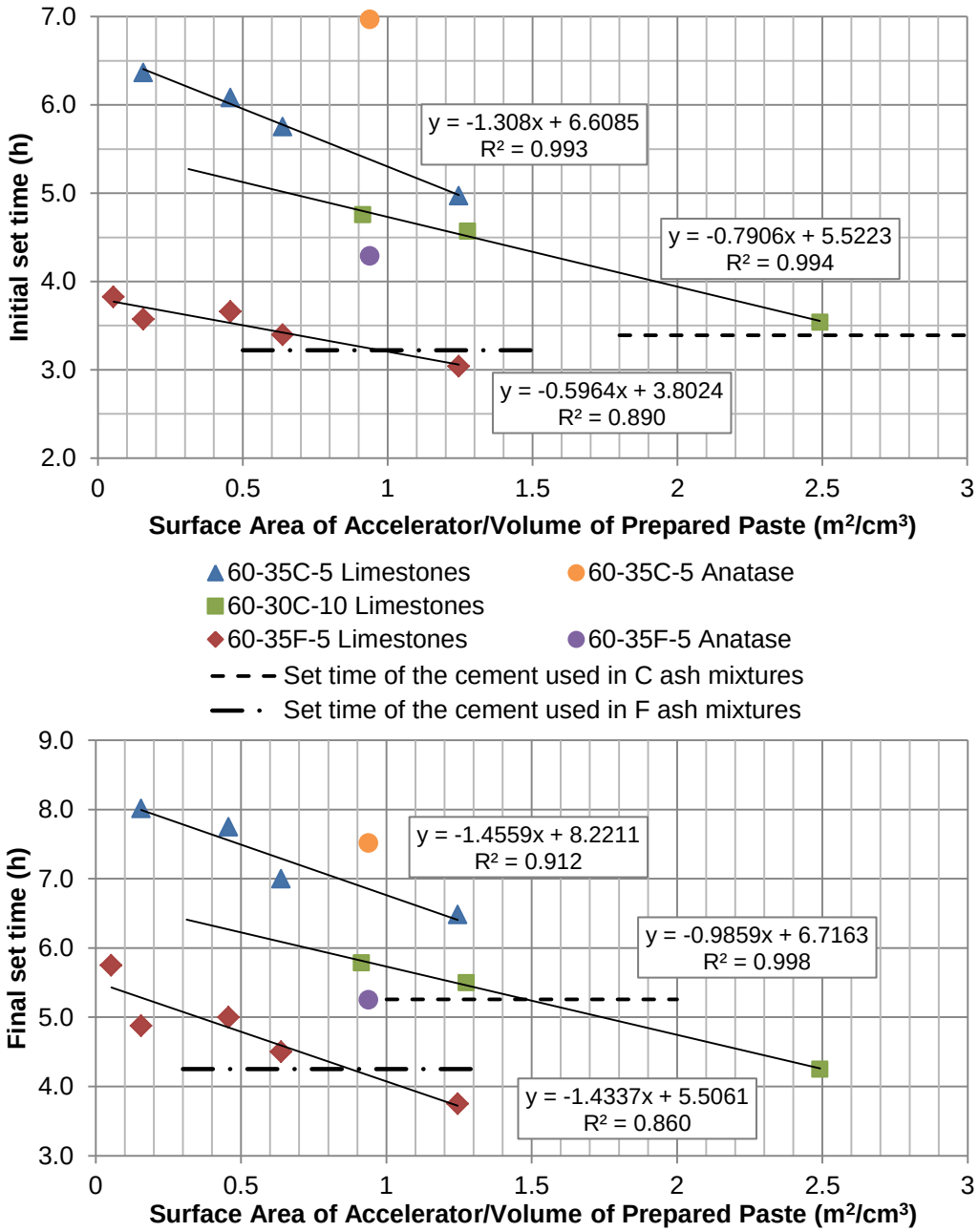


FIGURE 2 Heat flow and cumulative heat for a) the Class C and b) the Class F fly ash ternary mixtures. The short vertical lines indicate times of initial set.



481

482
483 **FIGURE 3 Correlation between initial (top) and final (bottom) setting times and surface**
484 **areas of the accelerators (powders).**
485

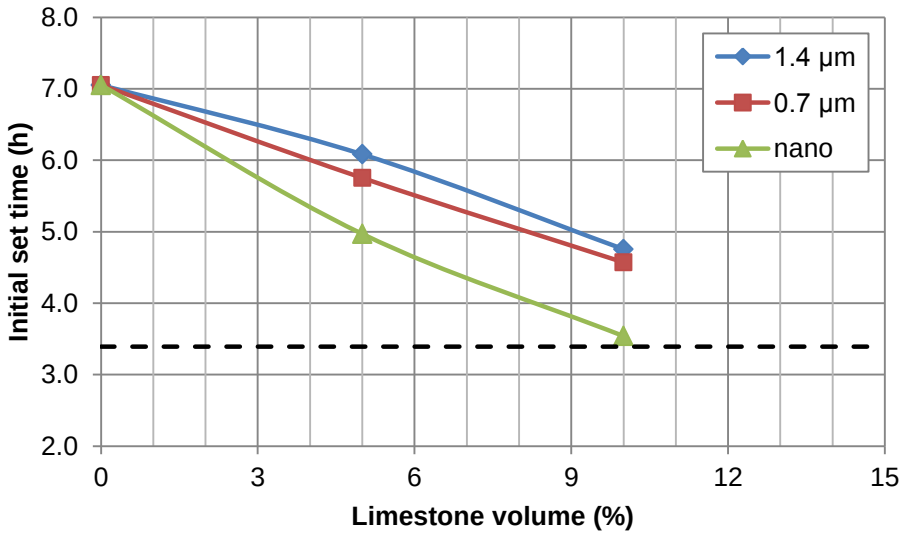


FIGURE 4 Relationship between initial setting times and limestone replacement level for Class C fly ash mixtures. The dashed horizontal line indicates the (desired) initial set time of the control 100 % OPC mixture.