

Anticipating the Setting Time of High-Volume Fly Ash Concretes Using Electrical Measurements: Feasibility Studies Using Pastes

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Abstract

One common concern limiting the proliferation of high-volume fly ash (HVFA) concrete mixtures is the significant delay in setting that is sometimes encountered in field concrete mixtures. While several methods to mitigate the delayed setting times of HVFA mixtures have been demonstrated, a related issue is the prediction of setting times in field mixtures, so that construction operations including finishing and curing can be anticipated and properly scheduled. This paper presents a feasibility study evaluating the employment of simple electrical measurements to predict the setting time of paste mixtures on which concurrent Vicat needle penetration testing was performed. Electrical, setting, and accompanying calorimetry tests are conducted at three different temperatures, each under quasi-isothermal conditions to minimize the confounding influence of temperature variation on the obtained results. Electrical resistance (or heat flow) measurements can be used to adequately predict a mixture's initial setting time for a wide variety of binary and ternary powder blends, prepared at a constant water volume fraction. However, a simple parametric study in 100 % ordinary portland cement pastes in which water content (water-to-cement ratio) is varied indicates that the relation between resistance trends and subsequent setting times is strongly dependent on the water content, as is also the case for the thermal measurements. This suggests that employment of this approach for field mixtures may require pre-determination of the resistance-setting time relationship for each mixture of interest (e.g., calibration) or at least that the on-site water content of the concrete mixture be assessed/verified by a separate measurement.

Keywords: Electrical properties; heat release; high volume fly ash; hydration; initial setting; resistance.

Introduction

While fly ash usage in concrete is slowly increasing, research continues to demonstrate the viability of high-volume fly ash (HVFA) concrete mixtures, in which fly ash volume fractions are two to four times the nominal 15 % that represents average current practice in the U.S. (Bentz et al. 2013a). One limitation in increased use of fly ash in concrete is its commonly perceived, and often achieved, detrimental impact on early-age properties, including undesirable delays in setting and low and slow strength development. The industry has developed a variety of

strategies for mitigating these detrimental characteristics of HVFA mixtures including lowering the water-to-cementitious materials ratio (w/cm) of the mixture, switching to an ASTM C150 Type III cement (ASTM 2012), using conventional accelerators, and/or replacing a portion of the fly ash with a fine $CaCO_3$ powder (Bentz et al. 2013a; Bentz et al. 2013b, De la Varga et al. 2014). From a contractor's point of view, in addition to reducing setting delays, it would be equally beneficial to the scheduling of construction operations if the initial setting of a field mixture could be anticipated. If a field mixture could be monitored on site and the initial setting time predicted in advance, the scheduling of construction crews and other resources could be optimized. In those cases where, due to unforeseen circumstances, setting of an HVFA mixture is substantially delayed (for more than 12 h in rare cases), having some indication that the mixture is in fact ultimately going to set and harden and when this might occur would be invaluable in helping to minimize uncertainties during construction and assuring that the "finishing window" is not inadvertently missed.

While onsite ultrasonic measurements can likely provide an adequate anticipation of setting (Subramaniam et al. 2005; Robeyst et al. 2011), the present study is concerned with evaluating the potential for using electrical measurements to anticipate setting. This is not a new topic by any means, as Shimizu (1928) proposed the use of electrical measurements for monitoring setting 85 years ago. More recently, Li et al. (2007) have proposed and investigated the determination of concrete setting using non-contact electrical resistivity measurements. Additionally, Mancio et al. (2010) have proposed that electrical measurements can be used to assess the water-to-cement ratio (w/c) or w/cm of field concretes. It should be kept in mind, however, that all of the concrete mixtures evaluated in this last study were prepared at a constant water content of 217 kg/m^3 , eliminating the possibility to investigate the influence of water volume fraction on the observed relationship between electrical resistivity and w/c .

Electrical transport in concrete is dominated by the characteristics of the solution-filled porosity (Snyder et al. 2000; Li et al. 2007; Mancio et al. 2010; Weiss et al. 2013; De la Varga et al. 2014). The measured sample resistivity can be related to the resistivity of the pore solution via:

$$\rho_{sample} = \frac{\rho_{solution}}{\phi\beta} \quad (1)$$

where ρ_{sample} is the measured resistivity for the sample, $\rho_{solution}$ is the corresponding resistivity of the pore solution, ϕ is the water-filled porosity (including both capillary and gel pores), and β is a connectivity factor (0 to 1). The product in the denominator is often represented by its equivalent form of $(1/F)$ where F is the formation factor (Weiss et al. 2013). As cement hydrates, all three terms on the right-hand side of equation (1) are changing simultaneously. As cement particles dissolve and ions go into solution, the resistivity of the pore solution is dramatically reduced; the lower the w/c , the greater the expected reduction in resistivity (all else being equal) (Mancio et al. 2010). This is subsequently counteracted by reductions in both porosity and pore connectivity due to the formation and growth of hydration products, the concurrent reductions in ϕ and β corresponding to an increase in formation factor. Thus, a representative pattern for electrical resistivity vs. time under isothermal conditions is an initial decrease, as ions go into solution (typically during the so-called dormant period of cement hydration), followed by a generally monotonic increase as the resistivity response becomes dominated by the ongoing reductions in porosity and pore connectivity, even as the concentration of ions in the pore solution and thus its conductivity (inverse of resistivity) may continue to increase. A constant water volume fraction

in concrete mixtures would be equivalent to a constant starting ϕ term in equation (1) and likely a very similar β term as well (depending on particles' sizes, flocculation, and spacing).

In their pioneering study, Li et al. (2007) have identified two critical parameters on a typical resistivity vs. time curve, namely the initial minimum in resistivity where the reduction in porosity and pore connectivity begin to dominate over decreases in pore solution resistivity and a second transition marking the time when the hydration kinetics transition from “the setting to the hardening stage.” The latter transition is identified by plotting the resistivity response on a logarithm time scale and noting the point of intersection of the two straight lines characterizing the early-age and longer term behaviors, respectively. For 11 different concrete mixtures, with the main variables being w/c (w/cm), fly ash incorporation, and the use of admixtures, they were able to establish relationships between the ASTM C403 (ASTM 2008a) times of initial and final setting and these two characteristic resistivity times. Final setting was related to the second transition time only ($R^2=0.990$), while initial setting was a linear function of both of the characteristic times ($R^2=0.895$). However, because the second transition time occurs up to several hours after initial setting (and sometimes even after final setting), one would have difficulty in using their presented relationships to anticipate setting times in the field. If only the former time of the resistivity minimum is used to anticipate initial setting, the relationship shown in Figure 1 is obtained, with a slightly reduced correlation relative to the results presented in (Li et al. 2007).

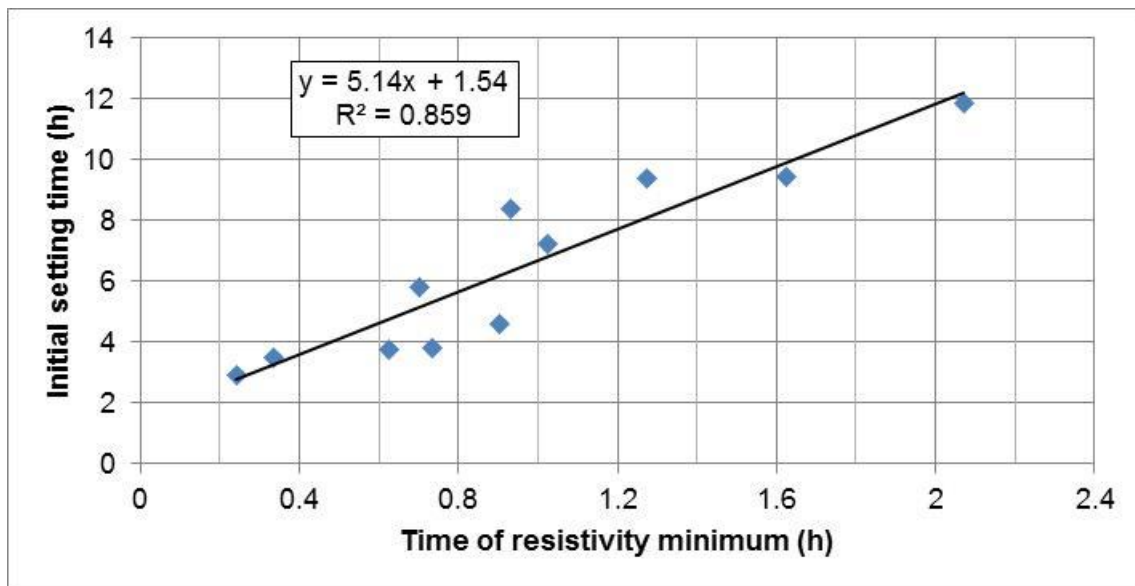


Figure 1. Data from Li et al. (2007) for initial setting time vs. the time of the resistivity minimum for their 11 concrete mixtures.

The goal in the present study is to build upon this previous research by investigating electrical, calorimetry, and setting measurements on a variety of (HVFA) pastes prepared and evaluated under quasi-isothermal conditions at three different temperatures.

Materials and Experimental Procedures

The electrical measurements presented here were largely performed in conjunction with a recent study on activation energy for setting and hydration in HVFA mixtures (Bentz 2014). As

such, the reader is referred to that reference for a more complete description of the materials employed. Basic powder components included a Type I/II cement, a Class C fly ash, a Class F fly ash, a fine calcium carbonate (CaCO_3) powder with a median particle diameter of about 1 μm , and a coarser CaCO_3 powder with a median diameter of about 17 μm (Bentz et al. 2013b; Bentz 2014; Tanesi et al. 2013). In the first phase of this study, paste mixtures were prepared with **constant volume fractions** of powder and water, based on a control 100 % ordinary portland cement (OPC) paste with $w/c=0.35$ by mass. As listed in Table 1, powder components and their volume fractions are indicated by the identifier assigned to each mixture (Bentz 2014). For example, the designation C30L10 would indicate a paste in which a total of 40 % of the cement has been replaced by volume, 30 % by Class C fly ash and 10 % by fine CaCO_3 . In a second phase of this study, five 100 % OPC paste mixtures were prepared using the same Type I/II cement, with w/c ranging from 0.30 to 0.50 in 0.05 increments.

Table 1. Powder Mixture Proportions (Volume) and Designations (Bentz 2014)

Designation	% Cement	% F ash	% C ash	% fine CaCO_3	% coarse CaCO_3	Investigated temperatures ($^{\circ}\text{C}$)
Control	100					15, 25, 40
L10	90			10		25
L10coarse	90				10	15, 25, 40
F40	60	40				15, 25, 25, 40
F30L10	60	30		10		
C40	60		40			25, 40
C30L10	60		30	10		15, 25, 40
F60	40	60				15
F45L15	40	45		15		15
C60	40		60			15, 25, 40
C45L15	40		45	15		15, 25, 40

For binary and ternary blends, all powder components were pre-blended for 30 min in a shaker-mixer to achieve a homogenous mixture. In the phase I study, pastes were prepared targeting three different final mixture temperatures (15 $^{\circ}\text{C}$, 25 $^{\circ}\text{C}$, or 40 $^{\circ}\text{C}$) using a high shear blender (without temperature control) and a combination of a reduced mixing temperature along with pre-cooling of the water and the powder blends. Final average mixture temperatures (with standard deviations) of 15.2 $^{\circ}\text{C} \pm 1.0$ $^{\circ}\text{C}$, 25.6 $^{\circ}\text{C} \pm 0.7$ $^{\circ}\text{C}$, and 37.9 $^{\circ}\text{C} \pm 1.1$ $^{\circ}\text{C}$ were achieved (Bentz 2014). From the 33 (11x3) mixtures prepared in the phase I study (Bentz 2014), impedance analysis was conducted on a subset consisting of 8 mixtures at 15 $^{\circ}\text{C}$, 9 mixtures at 25 $^{\circ}\text{C}$, and 7 mixtures at 40 $^{\circ}\text{C}$, as indicated in Table 1. In phase II, OPC pastes were prepared using a high shear blender with a built-in (water) cooling unit; a final paste temperature of 25.7 $^{\circ}\text{C} \pm 1.1$ $^{\circ}\text{C}$ was achieved and all testing in phase II was conducted at 25 $^{\circ}\text{C}$.

Isothermal calorimetry was conducted at each targeted temperature on small sealed paste specimens (in a glass vial), nominally about 5 g in mass. Data collection was usually initiated within 15 min to 30 min after first contact of water and powder, so that only part of the tail of the heat peak due to the initial dissolution of cement (and fly ash) upon contact with water was typically captured. For this technique, using similar materials, the average absolute difference between replicate specimens was measured to be 2.5×10^{-5} W/g (cement) with a maximum

absolute difference of 0.00011 W/g (cement), for measurements conducted between 1 h and 7 d after mixing (Bentz and Ferraris 2010). Automated Vicat needle penetration and impedance spectroscopy measurements were conducted in a temperature-controlled walk-in environmental chamber set at the relevant target temperature. Vicat measurements were performed at 15 min intervals using a commercial device, otherwise following the specifications of ASTM C191 (ASTM 2008b). According to the ASTM standard test method, the single laboratory precision for initial time of setting is 12 min. The initial time of setting was taken as the time when a penetration of 25 mm is first achieved and the results to follow are plotted in terms of penetration resistance, calculated as the quantity (40 – penetration), so that it will vary from low (0) to high (near 40) as setting proceeds, with a penetration resistance of 15 mm corresponding to initial setting.

Samples for impedance spectroscopy consisted of a cylinder (nominally 47 mm in diameter by 95 mm in height) of fresh cement paste placed in a sealed plastic container. Two 3 mm diameter threaded rods (spaced 30 mm apart) were inserted through the top plastic cap to a depth of about 45 mm to provide electrical contacts for the impedance measurements. An 18 mm long region of each inserted rod that contacted the top surface of the paste was insulated using a wrapping of electrical tape. This was performed to avoid any potential shorting of the circuit at this top paste surface due to accumulation of bleed water (particularly for $w/c \geq 0.45$ pastes). A commercial impedance analyzer with a 4-point setup was connected to the two terminals extending out of the measurement cell to evaluate the impedance response of the sample. Frequencies selected for the measurement of electrical impedance ranged from 100 Hz to 1 MHz, with specific values of (100, 278, 774, 2154, 5995, 16681, 46416, 129155, 359833, and 1000000) Hz, spaced uniformly on a logarithmic scale. Sample bulk resistance (R) was taken from the real component achieved when either the imaginary component crossed its zero axis or the imaginary component was closest to zero, as described in (Snyder et al. 2000). These frequency sweeps were conducted every 15 min, typically during the first 24 h of sample hydration. For measurements conducted during the first six hours, the standard deviation in the measured bulk resistance for replicate specimens prepared on different days varied between 0.5 Ω and 3.7 Ω (average coefficient of variation of 9.5 %). Although the measured resistance could have been converted to a sample resistivity by multiplying the resistance by an appropriate measurement cell (geometry) factor, in this study, the resistance values were used directly, as the cell geometry factor is a constant and the desired quantity is the time at which the slope (with respect to time, dR/dt) of the data changes. The assumption of isothermal conditions was examined for these impedance specimens by inserting a thermocouple into a companion $w/c=0.3$ paste specimen during its first 24 h of curing. The observed temperature rise up to the time of initial setting was less than 1 °C, confirming the assumption of quasi-isothermal conditions for the measured early-age impedance data.

Results and Discussion

Example raw data from the impedance frequency sweeps are presented in Figure 2 that provides a plot of the negative of the imaginary component vs. the real component at various times for a paste that was cast at 10:00 AM. The real resistance follows the behavior mentioned in the Introduction section, first decreasing slightly as ions dissolve into solution and then increasing dramatically as the capillary porosity and its connectivity are both reduced by the ongoing hydration process. In Figure 2, the first four scans cross or touch the zero axis, while the

fifth (10:32 PM) exhibits a minimum in the negative of its imaginary component that is just above the zero axis. It should be noted that while the procedure outlined in the previous section (taking the bulk resistance as the real component achieved when the imaginary component was closest to or equal to zero) was followed to determine the sample bulk resistance data to be presented subsequently, quite similar values and correlations would be obtained if a sufficiently high fixed frequency was used to obtain the bulk resistances, such as the 16681 Hz values in this study.

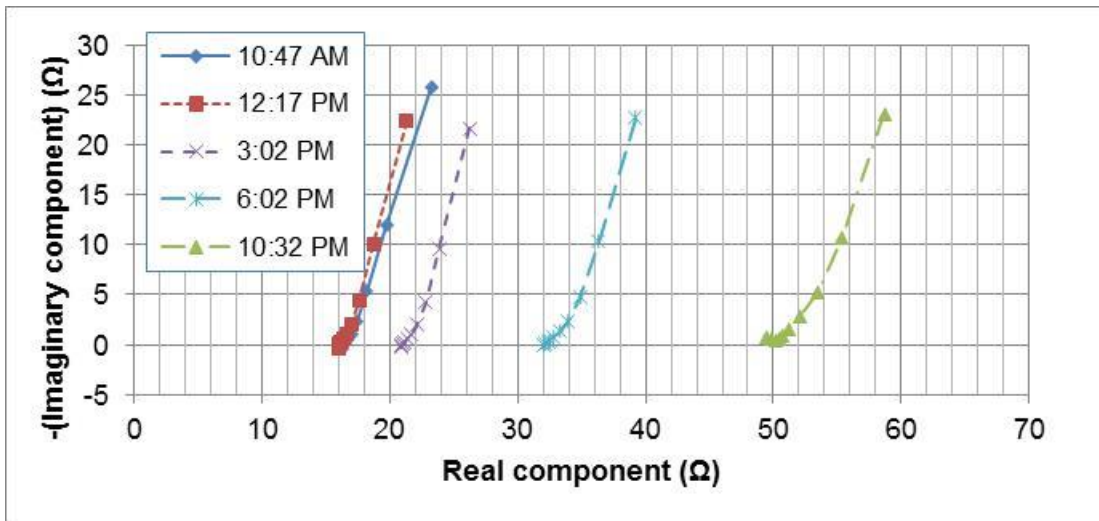


Figure 2. Impedance frequency scan results at various times for the F40 paste cured at 25 °C.

Using the so-determined bulk resistances, setting, calorimetry, and electrical results were compared to investigate potential predictive relationships between the latter two measurements and initial setting times. Example results for all three measurements and some of their derivatives are provided in Figures 3, 4, and 5 for the control, C40, and C60 pastes, respectively, chosen to bracket the observed range of setting times. Because the Vicat needle penetration only assesses a limited range of stiffness/strength, its curve appears almost as a step function in comparison to the more continuous nature of the electrical resistance and heat release results. The goal of the present effort is to develop and evaluate relationships between these latter two measurements and the initial setting time for the various mixtures being investigated. Once again, in phase I of the study, all of the mixtures being investigated have the same starting volume fractions of water and powders, although their powder compositions vary widely as shown in Table 1; likewise, their mass-based w/c or w/cm would also vary significantly.

In comparing the various curves shown in Figures 3 to 5, along with their equivalents for the other mixtures investigated in phase I, certain trends were identified. During the “dormant” period of cement hydration, little change occurs in the heat flow and resistance curves, with both quantities first decreasing following initial dissolution of the cement particles, then flattening out, before finally increasing more dramatically as hydration accelerates and initial setting occurs (Li et al. 2007). Past research has suggested that initial setting times relate well to the time of the (first) maximum rate of change in the heat flow curves (e.g., where $dheat/dt$ achieves its first maximum) (ASTM 2009; Bentz et al. 2009). Conceptually, this could correspond to the point when the hydrating cement particles begin to impinge upon one another, removing some surface area that was formerly available for reaction and initiating the building of the bridges that

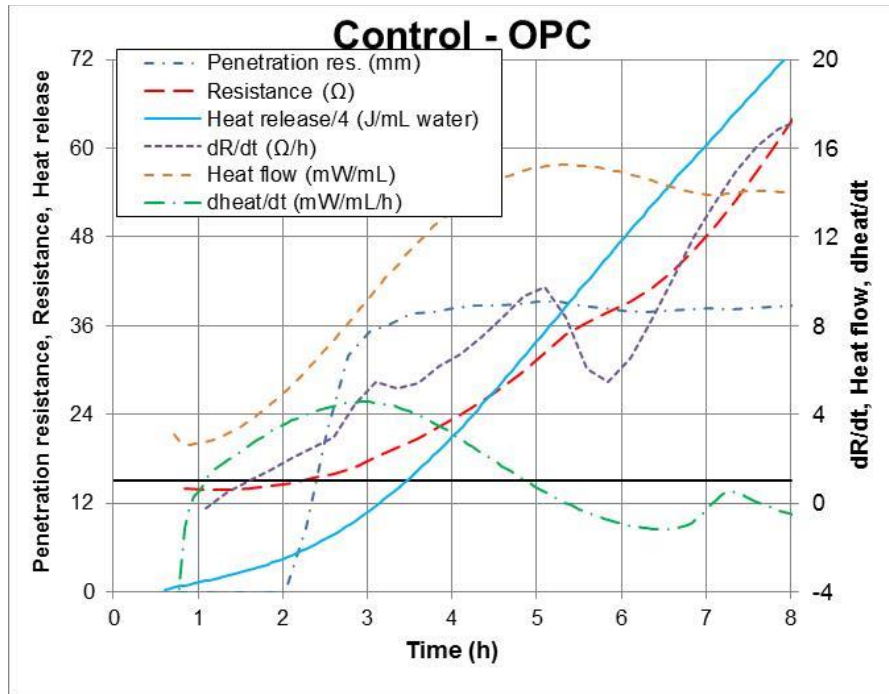


Figure 3. Comparison of heat release, electrical resistance, and their time-derivatives with needle penetration resistance as a function of time for the control OPC paste with $w/c=0.35$, cured under sealed/open conditions at 25 °C. The solid black line indicates initial set at a penetration resistance of 15 mm. Note that the presented heat release data have been divided by 4 in order to fit well on the same graph with the other variables.

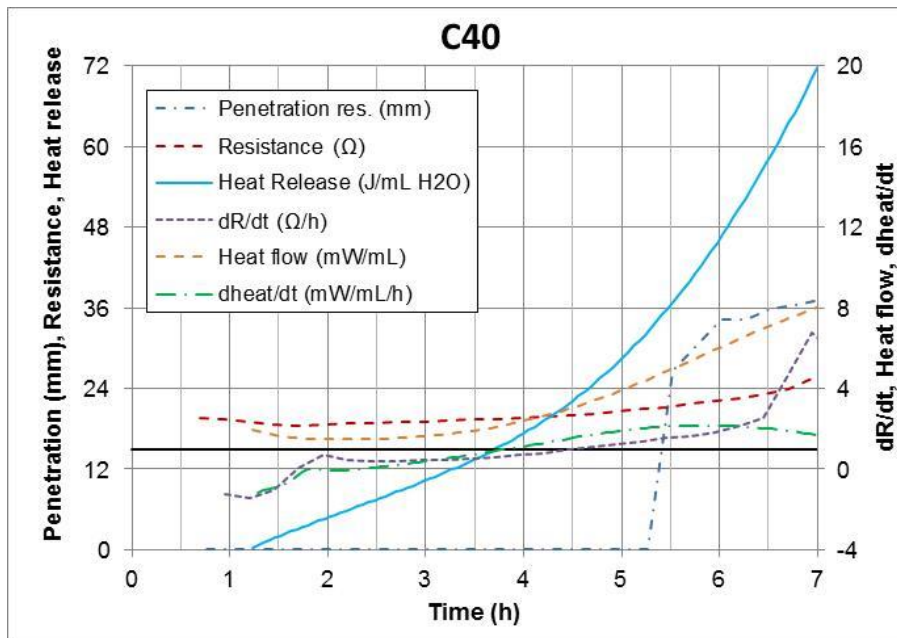


Figure 4. Comparison of heat release, electrical resistance, and their time-derivatives with needle penetration resistance as a function of time for the C40 HVFA blended cement paste, cured under sealed/open conditions at 25 °C. The solid black line indicates initial set at a penetration resistance of 15 mm.

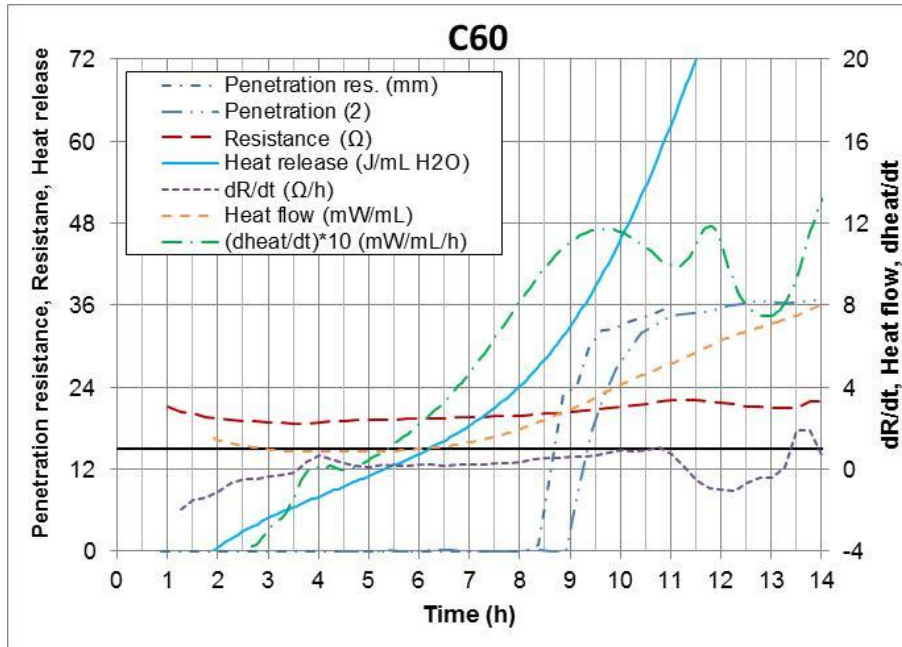


Figure 5. Comparison of heat release, electrical resistance, and their time-derivatives with needle penetration resistance as a function of time for the C60 HVFA blended cement paste, cured under sealed/open conditions at 25 °C. The solid black line indicates initial set at a penetration resistance of 15 mm. Replicate penetration resistance results are shown to provide an indication of variability. In this case, $dheat/dt$ has been rescaled by a factor of 10.

will constitute the setting process (Bentz 2007). In this case, the lost surface area could lead to the observed maximum in heat flow rate, so that this characteristic time could perhaps be used to predict initial setting.

Figure 6 provides a plot of the time of this first maximum in heat flow rate ($dheat/dt$ in Figures 3 to 5) vs. the measured initial setting time and indeed a good linear relationship is observed between the two measures for the phase I mixtures prepared with a constant volume fraction of water. Even though there is an acceptable correlation between this heat release parameter and initial setting times in phase I, unfortunately, the former could not be used to **anticipate** the latter, as they occur in the same basic time window, with initial setting sometimes even preceding the time of the maximum rate of heat flow. Furthermore, in the phase II study, as shown by the results in Table 2 and included in Figure 6, this correlation deteriorates when the water content (or equivalently w/c for 100 % OPC mixtures) of the mixtures is varied. For the 5 different w/c ratios investigated in phase II, while their setting time range is 2.9 h, the range in their times of maximum rate for heat flow is only 0.7 h, more than a factor of four times less. The limited results in Figure 6 suggest that a separate calibration curve might be needed for each individual water volume fraction to successfully predict setting times from such thermal measurements.

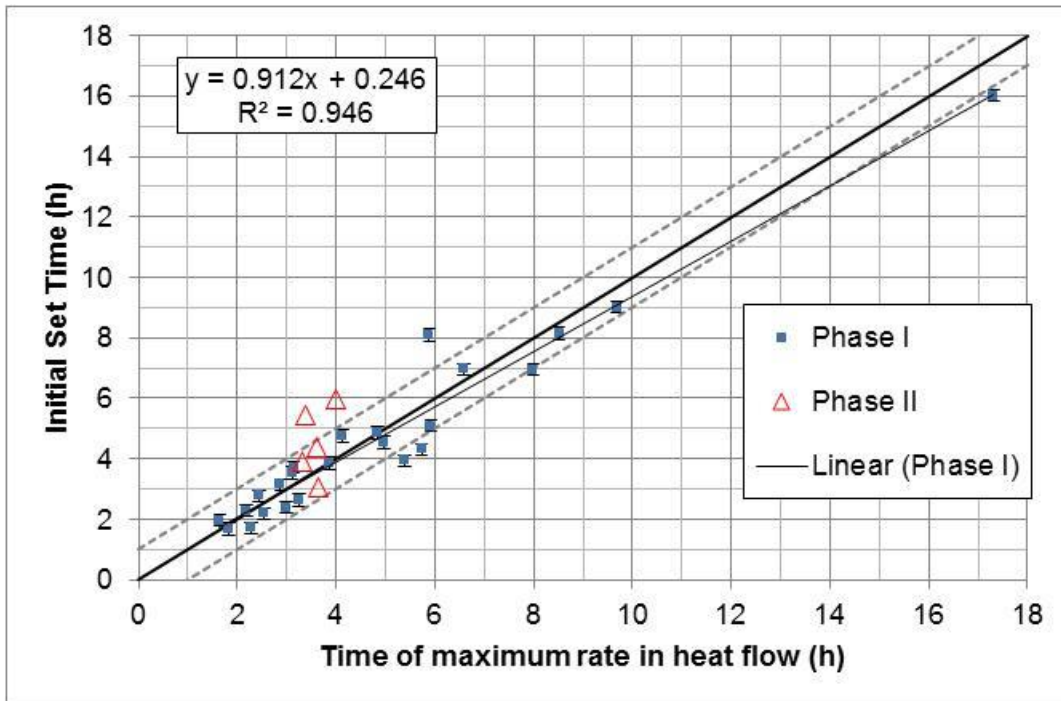


Figure 6. Measured initial setting time vs. time of maximum rate in heat flow for the 24 phase I and 5 phase II mixtures. The thicker solid line indicates a one-to-one relation, while the thinner solid line indicates the best fit linear relationship limited to the phase I mixtures, as shown in the upper left legend box. The two dashed lines represent a variation of ± 30 min from the one-to-one relation.

Table 2. Results for pastes of variable w/c in the phase II study.

w/c	Initial setting time (h)	Time for $dR/dt=0$ (h)	Resistance criteria time (h)	Heat flow minimum (h)	Time of maximum rate in heat flow (h)
0.30	3.06	1.12	1.57	1.11	3.63
0.35	3.91	1.01	1.97	1.13	3.33
0.40	4.39	1.08	1.08	1.05	3.62
0.45	5.43	1.17	1.70	1.24	3.38
0.50	5.96	1.28	2.47	1.20	3.99

In the hopes of anticipating setting times well before they occur, the relationship between setting times and the times of minima in either the heat flow or electrical resistance curves (Li et al. 2007) were investigated next. First, as shown in Figure 7 for the phase I mixtures, it should be noted that the two sets of minimum times are correlated, but they are not one-to-one, suggesting that one might provide a better correlation with subsequent setting times than the other. When initial setting times are plotted against each of the two minima (Figure 8), the correlation is slightly better for the heat flow minimum than for the resistance minimum time. For either approach, the behavior for the phase II mixtures appears unique from that for phase I, illustrating the significant influence of water content (w/c) on the resistance-heat flow-setting relationship. The data from concrete mixtures obtained by Li et al. (2007) is also included in Figure 8. It is roughly parallel to, but distinct from, the paste data obtained in this study, as a different method was used to evaluate setting in each case (ASTM C403 vs. ASTM C191) and

the resistivity data in the previous study (Li et al. 2007) was obtained at a fixed measurement frequency of 1000 Hz.

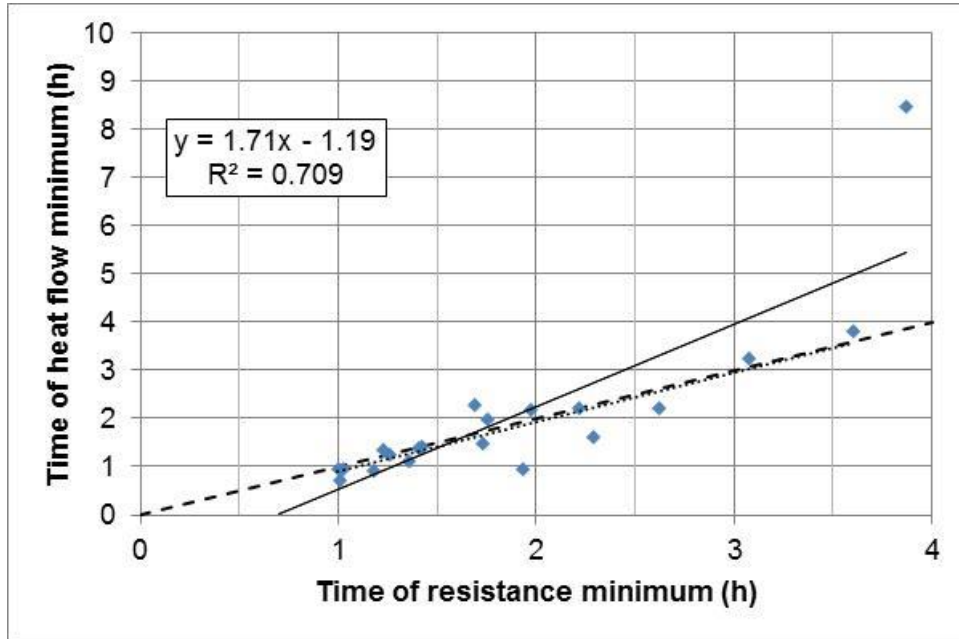


Figure 7. Relation between times of minimum heat flow and minimum resistance for the phase I mixtures. Dashed line indicates a one-to-one relation, solid line indicates the best linear fit (see legend for fit parameters), and dotted line indicates best fit with data point at (3.9, 8.5) considered as an outlier.

An attempt was made to improve upon the correlation exhibited in Figure 8 by further examining the dR/dt curves for the phase I mixtures. For many of the HVFA mixtures (with or without fine CaCO_3), it was observed that after the dR/dt curve crossed its zero axis, it would flatten and exhibit a subsequent minimum before increasing again (see Figures 4 and 5 for examples). This could be due to some retarding influence of the fly ash present in the HVFA mixtures temporarily reducing hydration rates and further delaying setting times. Based on this observation, a resistance time criteria was established that corresponds to the maximum time of either the minimum in resistance ($dR/dt=0$) or the subsequent minimum in dR/dt itself (when present). A plot of the initial set time vs. this resistance criteria is provided in Figure 9. For the phase I mixtures, the correlation for the linear fit is much improved to 0.97 and more than 50 % of the experimental data for initial setting time falls within 30 min of the resistance-predicted (anticipated) value. Only two experimental setting times from the phase I paste mixtures deviate more than 1 h from their anticipated values. The two phase II mixtures prepared with a similar or lower water content as the phase I mixtures (e.g., those with w/c of 0.30, 0.35) exhibit reasonable agreement with the fitted linear relationship. However, the three phase II mixtures with a higher w/c of 0.40 and greater (higher water content) deviate significantly from the established relationship, lying well above it. Once again, this suggests that separate calibration curves of initial setting time vs. the resistance criteria time would need to be established as a function of the water content (volume fraction) of the concrete mixtures.

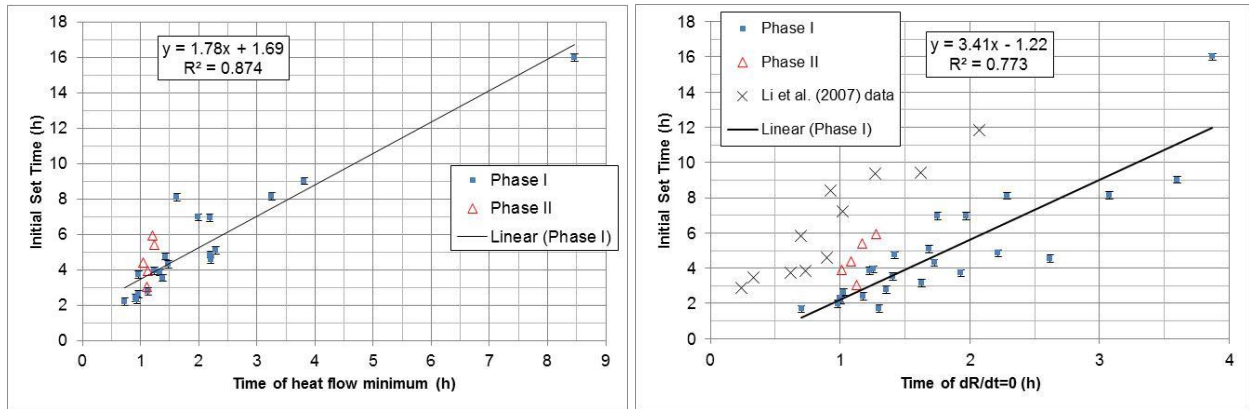


Figure 8. Plots for initial set time vs. minimum times for heat flow (left) and resistance (right) for the phase I mixtures, along with their best linear fit. In comparing the two plots, please note that their x-axis time scales are different. Error bars on phase I data points indicate a variation of ± 12 min as per the ASTM C191 standard (ASTM 2008b).

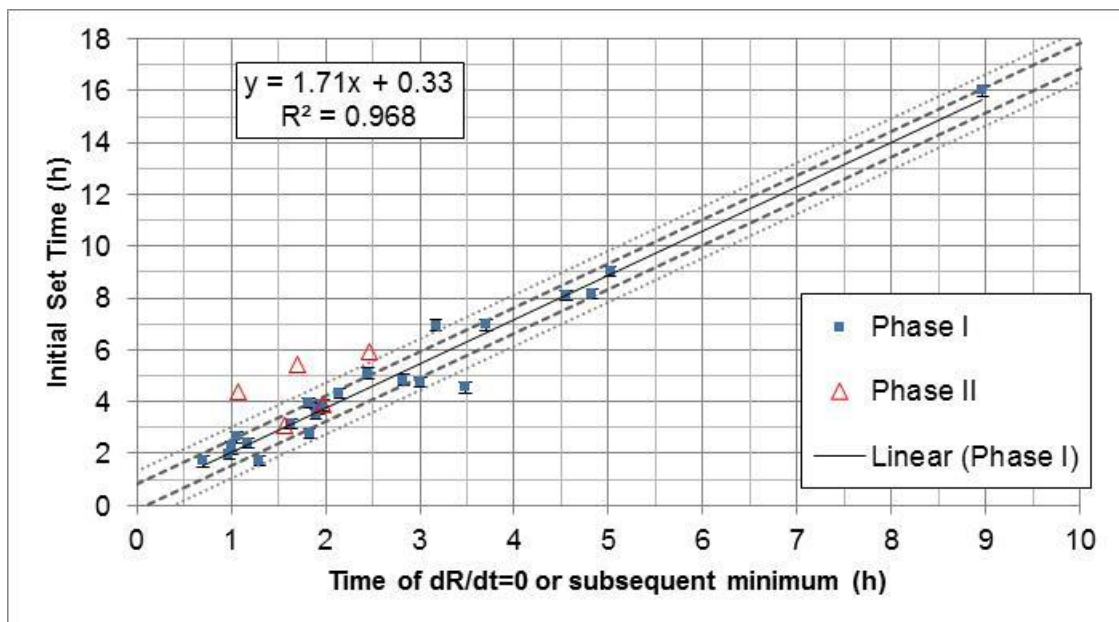


Figure 9. Initial set time vs. resistance criteria time for the phase I and phase II paste mixtures. The solid line indicates the best fit linear relationship for the phase I mixtures only. The heavy dashed lines indicate a variation from the predicted values of ± 30 min, while the light dotted lines indicate a variation of ± 1 h.

The results in Figures 8 and 9 indicate that initial setting times could be anticipated at least 90 min in advance for setting times of 3 h and beyond. As mentioned in the Introduction section, this onsite sensing technology would be most applicable to HVFA concrete mixtures where setting has been unacceptably and likely unexpectedly delayed for multiple hours. In those cases, any of the predictive approaches shown in Figures 8 and 9 would offer an improvement over having no information on when initial setting will finally occur. While those in Figure 8 might sometimes underpredict or overpredict the correct initial setting time by 1 h to 2 h, the results in Figure 9 indicate that this underprediction or overprediction should be limited to about 1 h in nearly all cases (at a constant water content). Obviously, while underpredicting the

setting time and having to remain on the job site until finishing can be performed is not ideal, overpredicting the setting time and finding a concrete that can no longer be properly finished is truly undesirable. Further research will be needed to evaluate these predictions on field concretes being cured under variable environmental conditions, using portable measurement equipment.

Conclusions and Prospectus

Similar to the conclusions first reached by Li et al. (2007), this study has indicated a promising potential for anticipating initial setting times in HVFA concrete mixtures using measurements of electrical resistance, based on experiments conducted at three different temperatures. The particular influence of water content (the initial ϕ term in equation (1)) has been highlighted and, in practice, it is likely that calibration curves for each water volume fraction of interest may need to be determined prior to implementation as a predictive or quality assurance tool for field concretes. Isothermal calorimetry measurements can provide anticipations of initial setting time that are similar in accuracy to those provided by electrical measurements, but it may be difficult to maintain isothermal conditions at the construction site.¹ Much remains to be done prior to the practical implementation of this sensing technology, but the initial results are promising and merit further research on this topic.

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¹ Semi-adiabatic calorimetry or calorimetry conducted under temperature conditions matching those experienced at the construction site may be more appropriate for anticipating initial setting times in the field, but were not evaluated in the present study.

² 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.

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