ELSEVIER

Rheological Changes Associated with Setting of Cement Paste

Leslie J. Struble* and Wei-Guo Lei†
*Department of Civil Engineering and †Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois

A method is described in which the yield stress of portland cement paste is determined from its creep/recovery behavior measured using a constant stress rheometer. As long as the applied stress does not exceed the yield stress, yield stress can be determined as a function of time on a single specimen without breaking down the microstructure. The early hydration is seen to strengthen the interparticle bonding within the flocculated structure, hence increasing the yield stress. Time evolution of the measured yield stress shows two regions, the first in which the yield stress increases slowly, and the second in which the yield stress increases rapidly. These correlate with the induction period and the acceleratory period, and the transition to a rapid increase in yield stress corresponds to the initial setting time. Reducing the water:cement ratio caused this initial setting time to be reduced. ADVANCED CEMENT BASED MATERIALS 1995, 2, 224–230

KEY WORDS: Creep, Floculation, Hydration, Induction period, Initial set, Paste, Rheology, Set, Yield stress

To process (mix, consolidate, finish) fresh concrete, it is necessary to predict and control its flow behavior. It is often assumed that the rheological behavior of concrete is strongly influenced by the behavior of fresh cement paste. Clearly, the early cement hydration reactions and their associated microstructural changes (i.e., setting) play a major role in controlling the flow behavior of concrete. Unfortunately, we lack a detailed understanding of the early microstructural transformations, despite the fact that the early hydration reactions have been studied for many years. Only with a clear picture of cement hydration and setting can we fully predict and control the performance of concrete.

Setting is a poorly defined phenomenon, both macroscopically and microstructurally [1]. Setting is the onset of rigidity, the initial step in the gradual transformation of fresh cement paste or concrete from a fluid to a solid. Setting is usually measured as resistance to penetration (using a Vicat or Gillmore needle for cement paste or mortar, or the Proctor needle for mortar sampled from concrete). At initial set, the concrete can no longer be properly handled and placed; and at final set, it begins to develop useful strength. The levels of penetration corresponding to initial and final set are entirely arbitrary, and the tests provide no fundamental knowledge about the chemical and microstructural processes related to setting.

It is important to understand both the chemical (hydration) and physical (microstructural) changes associated with setting. For a normal cement, setting is generally attributed to the formation of C-S-H [2]. However there is no direct experimental evidence to link setting to specific hydration reactions, in part because setting remains an empirical parameter.

Because setting is concerned with the development of rigidity in an initially fluid material, it is assumed to be part of rheology, the study of flow. However, we must first consider what specific rheological parameters are associated with setting. The flow of cement paste approximates plastic (i.e., Bingham) behavior [3] and is therefore characterized by its yield stress (below which the suspension displays solid-like behavior) and its plastic viscosity ($d\tau/d\dot{\gamma}$). The plastic viscosity depends largely on the volume of solid particles and how densely they are packed. The microstructure most commonly responsible for a high yield stress is the three-dimensional network that often forms due to flocculation. The yield stress reflects the extent of this flocculation and the strength of the attractive interparticle forces responsible for the flocculation.

Hydration is known to increase both yield stress and plastic viscosity [4]. It presumably increases plastic viscosity only insofar as it increases the volume fraction of solid material. It is yield stress that is expected to be particularly sensitive to hydration reactions. To the extent that the early hydration products cause the cement particles to be bonded more strongly together or increase the number of interparticle bonds, hydration

Address correspondence to: Leslie J. Struble, Department of Civil Engineering, University of Illinois at Urbana-Champaign, 219d Newmark Laboratory, MC-250, 205 North Mathews Avenue, Urbana, IL 61801-2352.
Received August 10, 1994; Accepted October 24, 1994

ISSN 1065-7355/95/$9.50
SSDI 1065-7355(95)00017-L

is expected to increase the yield stress. Setting corresponds to the development of a substantial yield stress.

A major difficulty in measuring yield stress of flocculated suspensions is their sensitivity to shear history. Yield stress is typically estimated by measuring stress at various strain rates (i.e., a flow curve) and extrapolating to determine stress at zero strain rate. Thus, it is necessary to cause the suspension to flow in order to determine yield stress. To achieve such flow, there must be a major breakdown in microstructure; particles that were bonded together must become separated. This breakdown means that subsequent yield stress measurements are very low, at least until the microstructure has been reestablished. In the case of hydrating cement, this breakdown means that the yield stress cannot be measured repeatedly on a single specimen.

Recent advances in rheometry may allow one to estimate yield stress without exceeding its value, thereby avoiding the microstructural breakdown associated with measurement of a flow curve. One such advance is the use of a constant stress rheometer to measure creep and recovery behavior. Struble and Schultz [5] demonstrated that the creep/recovery behavior of cement paste undergoes a transition from solid-like behavior at low stress to liquid-like behavior at high stress, and the stress level associated with this transition agrees well with the yield stress estimated from flow curves and from oscillatory shear data for pastes with little hydration. The objective of the present work was to explore whether the creep/recovery method could be used to monitor the very early strength development of cement paste.

Experimental

The portland cement was a commercial Type I (obtained from Essroc Materials Inc.): SiO_2, 20.4%; Al_2O_3, 5.2%; Fe_2O_3, 3.7%; CaO, 63.1%; MgO, 2.8%; SO_3, 2.6%; total alkalies, 0.55%; loss on ignition, 1.3%; Blaine fineness, 362 m^2/kg. The cement was passed through a 74-μm sieve to remove any lumps and then was used without further preparation. Deionized water was used throughout.

The initial setting time was determined for cement paste according to ASTM C 191, Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle. The penetration depth of the Vicat needle is measured and initial setting is reached when the needle penetration is 25 mm. The test specifies that the paste have a so-called normal consistency, which requires a very low water:cement ratio, determined according to ASTM C 187, Standard Test Method for Normal Consistency of Hydraulic Cement. For the cement used here, the water:cement ratio (w:c) was 0.24. The Vicat test was carried out at room temperature (ca. 25°C).

An isothermal calorimeter (Digital Site Systems K2000 Calorimeter) was used to monitor the hydration rate of paste and to determine the time at which the induction period ends. Paste (w:c = 0.45) was mixed by hand and then transferred, as quickly as possible, to calorimeter cells, using 8 to 10 g paste in each cell. The cells were immediately immersed in a water bath, which was maintained at 25 ± 0.1°C. Heat flow was measured using solid state thermopile-type sensors, which were calibrated with resistance heaters. Data were collected using a personal computer.

Pastes for rheological measurements were mixed by hand (10 g cement with the appropriate amount of deionized water) and then transferred to the rheometer where they were mixed at a high shear stress (200 Pa for 45 seconds) to ensure a common, homogeneous initial microstructure [5]. Pastes were then allowed to hydrate in the rheometer for some length of time, after which rheological measurements were begun.

The rheological measurements utilized the same computer-operated controlled stress rheometer (Bohlin CS Rheometer) described in ref 5. All measurements utilized Couette (cup and bob) geometry. The radius of the bob was 7.0 mm, and the gap between cup and bob was 0.7 mm. Both cup and bob had smooth surfaces. The temperature was maintained at 25°C using a circulating water bath. A solvent trap was used to prevent evaporation of water during testing. The desired stress was applied for 30 seconds while creep strain was measured, then the applied stress was held at zero for 30 seconds while recovery strain was measured.

Results

Figure 1 shows the penetration depth of the Vicat needle versus hydration time in paste of normal consistency (w:c = 0.24). The initial setting time was found to be 152 minutes. This graph also shows how abruptly the penetration depth changes during initial setting.

The end of the induction period was determined using isothermal calorimetry. The results (Figure 2) show a rapid initial peak followed by an induction period, during which the rate of heat flow is quite low, and then show an acceleratory period, during which there is a progressive increase in heat flow. The end of induction period, the time at which dQ/dt begins to increase, was 130 minutes.

Yield stress was determined from creep/recovery curves at various levels of applied stress. As reported previously [5], the paste transforms from a solid to a liquid over a narrow stress interval, and the stress level

Advn Cem Bas Mat
1995;2:224–230

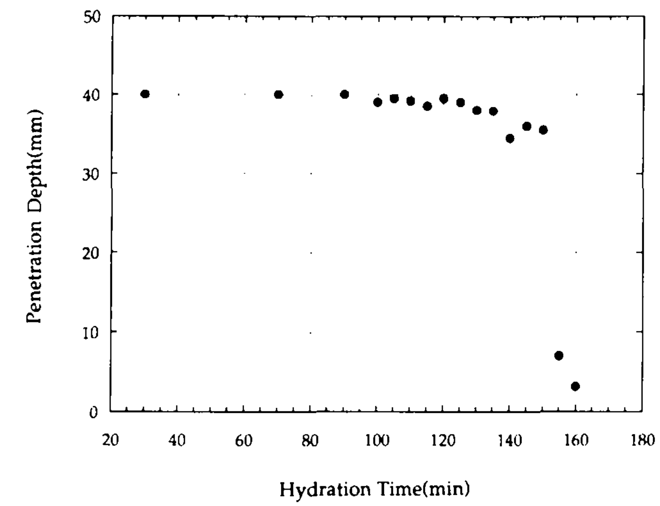

FIGURE 1. Initial setting time of cement paste (w:c = 0.24) determined using the Vicat needle.

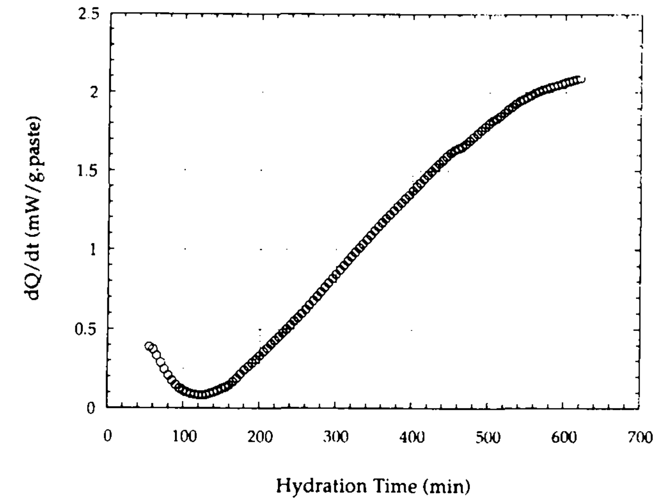

FIGURE 2. Rate of heat flow (*dQ/dt*) of cement paste (w:c = 0.45) versus hydration time.

of this transformation is a measure of the yield stress. Figure 3 shows the creep/recovery behavior after a hydration time of 30 minutes. The behavior was similar in most respects to that reported previously [5]. At an applied stress of 15.8 Pa, the paste behaved as an elastic solid; creep compliance was very low (4×10^{-5} Pa^{-1}), creep compliance included both an elastic strain and a retarded elastic strain, and recovery was somewhat slow. At a slightly higher applied stress of 16.5 Pa, the paste behaved as a viscous liquid (alternatively one might characterize it as a weak plastic solid): the creep compliance was very high, creep compliance increased in a reasonably linear manner with time (reaching 55 Pa^{-1} after 30 seconds), and there was no recovery. Therefore, the yield stress in this case was between 15.8 and 16.5 Pa.

Yield stress was determined for specimens of various ages to determine how it changes with time. The creep/recovery behavior was measured for a number of separate specimens at each hydration time in order to define accurately the stress level at which the transition from solid to liquid occurred. (These measurements required 5 to 15 separate specimens for each hydration time.) Results are shown in Figure 4. The yield stress was found to increase slowly during the first 2 hours, after which it increased much more rapidly. The time at which the yield stress increased in slope was 125 minutes, very close to the end of the induction period as determined from calorimetry measurements and similar to the initial setting time determined using the Vicat needle.

A key objective of this work was to explore whether the creep/recovery technique would allow sequential measurements of yield stress on a single specimen. In other words, could we determine the yield stress by applying a stress lower than the yield stress and

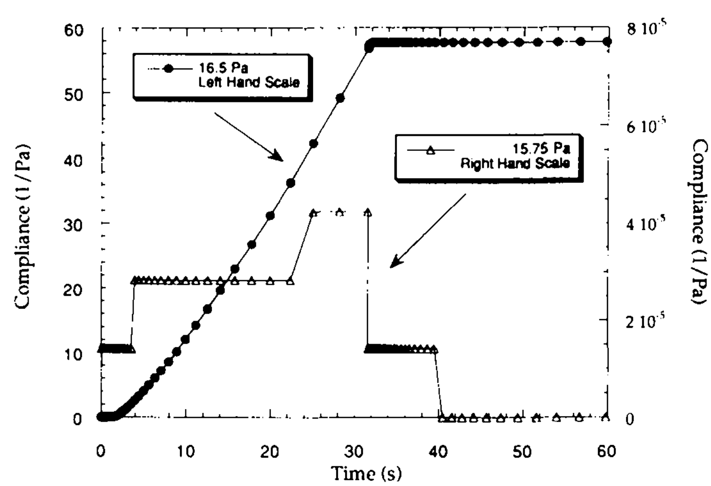

FIGURE 3. Creep and recovery behavior of cement paste (w:c = 0.45) after 30 minutes hydration, measured discretely at two stress levels.

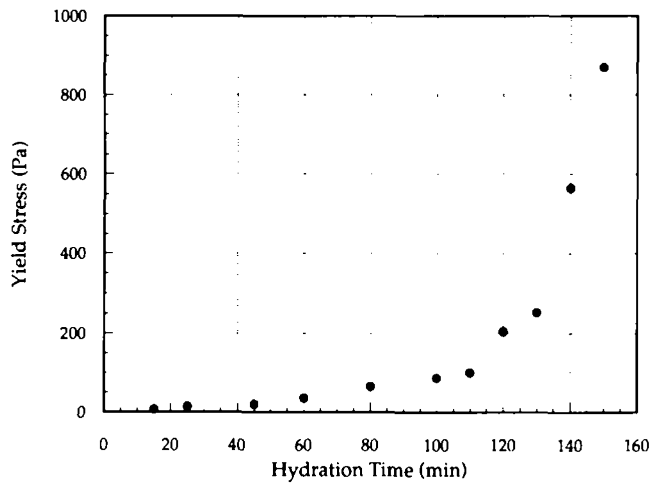

FIGURE 4. Yield stress of cement paste (w:c = 0.45) as a function of hydration time using discrete measurements on separate specimens.

thereby avoid the structural breakdown associated with flow? It turned out that careful analysis of the creep behavior allowed us to determine when the applied stress was close to the yield stress. When the applied stress was well below the yield stress, the paste showed elastic behavior (creep compliance was fully instantaneous and recovery was instantaneous and complete). As the applied stress approached the yield stress, the behavior became increasingly viscoelastic (creep compliance increased with time and a considerable portion of the creep compliance was not recovered, as shown in Figure 5). Creep compliance levels were still quite low; specimens did not flow in the sense that the specimen in Figure 3 flowed at the higher stress level, but they were beginning to show viscoelastic behavior. The stress levels at which the paste showed a modest degree of viscous response provided an approximate measurement of yield stress. After each measurement, the specimen was allowed to hydrate further, then the creep/recovery measurement was repeated to measure the new yield stress. Great care was taken to keep the specimen from flowing. If the applied stress exceeded the yield stress and the specimen flowed, it could not be used for subsequent measurements.

Figure 6 shows the time evolution of the yield stress measured sequentially on a single specimen, with the discrete yield stress measurements from Figure 4 plotted for comparison. The discrete values provide a more precise measurement of yield stress than the sequential values, but the two agree well. At 150 minutes, the sequentially measured yield stress values abruptly decreased to about zero and then began to increase again. The reason for this behavior is that the preceding applied stress exceeded the yield stress of the specimen and caused it to flow. The flow caused a structural breakdown, after which the paste had a very low yield stress. Reflocculation of the broken structure and additional hydration were required to reestablish links between particles and cause the yield stress to grow

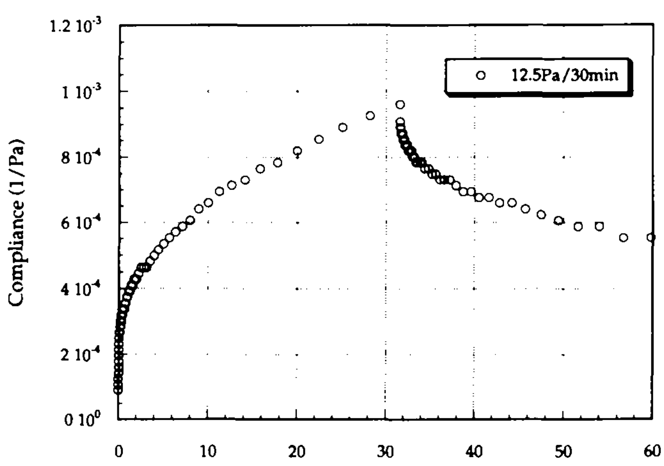

FIGURE 5. Creep and recovery behavior of cement paste (w:c = 0.45) after 30 minutes hydration, one of a series of sequential measurements at various hydration times.

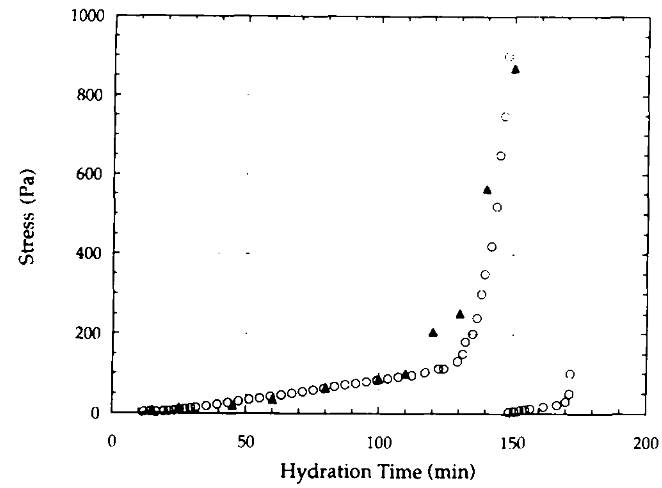

FIGURE 6. Yield stress of cement paste (w:c = 0.45) as a function of hydration time, showing sequential measurements on a single specimen, and discrete measurements on separate specimens (from Figure 4).

again. Such behavior when the yield stress is exceeded provided evidence that measurements using an applied stress that does not exceed the yield stress do not seriously perturb the microstructure and that the approach used here of sequential measurements below the yield stress is a valid way to probe rheological changes associated with early hydration and setting.

The effect of w:c was explored in one additional experiment. Figure 7 shows the sequentially measured yield stress for pastes with w:c 0.40 and 0.45. As the w:c decreased, the initial setting time also decreased.

Discussion

The creep/recovery technique offers a considerable advantage over flow curves for determining the yield stress of flocculated suspensions. Concentrated cement paste has a three-dimensional flocculated structure [3,6–8], as indicated by its plastic or pseudoplastic flow behavior. Paste commonly shows shear thinning above the yield stress, an indication that the microstructure is progressively breaking down under shear. As with any flocculated suspension, the flow behavior of cement paste is very dependent on its shear history and on the rate at which flocs reform after shearing has ceased. The yield stress is usually determined from a flow curve obtained in going from high shear rate to low shear rate [4], but the measured value depends on other specific experimental procedures as well. Thus, a flow curve is not an accurate way to determine yield stress. With hydrating cement, the flow curve is even less reliable because flow breaks down the delicate hydrated microstructure. Creep/recovery seems to be the best among the available techniques for determining yield stress because it causes only minimal distortion of the microstructure [9].

Although the yield stress did not appear to be affected by shear history, other aspects of the creep/

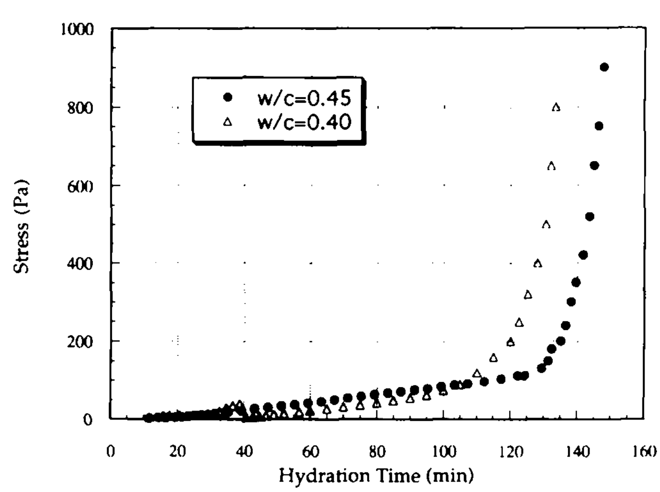

FIGURE 7. Yield stress of cement paste as a function of hydration time using sequential measurements on a single specimen, showing paste at w:c = 0.40 and w:c = 0.45.

recovery behavior were affected by previous shear. The viscoelastic creep and recovery behavior observed in sequential measurements at stress levels near the yield stress (Figure 3) was only observed for specimens that had already been loaded. On first loading, specimens always showed a more highly elastic response, even at stress levels only just below the yield stress (Figure 5). We plan to explore this behavior further.

Other rheology studies have limited shear measurements to very low strains or low strain rates in order to minimize the microstructural changes caused by flow. For example, Min et al. [10] recently used a low strain-rate technique and defined yield stress as the stress overshoot. The yield stress determined in this way, although it reflects the resistance of the paste to flow, is probably still associated with some structural breakdown and therefore does not reflect the microstructure of the quiescent paste.

Another rheological parameter that could be used to study setting is the storage modulus, determined using low-amplitude oscillatory shear. Storage modulus reflects directly the interaction forces between particles, and thus should provide a suitable probe to measure changes in bonding between cement particles. However, it is difficult to measure for cement paste. The critical strain of flocculated cement paste is very small, on the order of 10^{-4}, and the storage modulus is quite high, about 10 kPa [11]. Measurements under these conditions reach or exceed the limits of most rheometers. For this reason, we have focused on creep/recovery rather than oscillatory shear for studying microstructural changes associated with early hydration reactions in cement paste.

The present research suggests that yield stress measured without causing structural breakdown is a microstructure sensitive parameter and a characteristic material property of the quiescent cement paste.

The yield stress development shown in Figures 4–7 is what one would expect for paste during its early hydration time. During the induction period, the yield stress increases slowly. Once the acceleratory period begins, the yield stress increases much more rapidly. The transition from the initial slow increase in yield stress to the more rapid increase occurs at about the same time as the increase in hydration rate that characterizes the end of the induction period, measured using calorimetry. The transition also correlates reasonably well with the initial setting time measured using the Vicat test. Yield stress, when measured in this way, can be used to characterize the setting behavior of cement paste. To our knowledge, this is the first time that rheological measurements have been successfully used to probe the setting of cement. It is important to note that yield stress reflects changes in microstructure, whereas the induction period comes about due to a change in chemical kinetics. Setting is a microstructural, not a chemical, phenomenon; in order for set to occur, it is necessary but not sufficient that hydration take place.

One result of this study is that setting time measured using the yield stress decreased when w:c was reduced. Therefore, it is expected that the normal consistency paste (w:c = 0.24) used for the Vicat test would have a very short setting time. It is perhaps fortuitous that the setting time determined by the Vicat test on low w:c paste agreed so well with the setting time measured by yield stress on high w:c paste. We did try to measure yield stress of normal consistency paste, but it exceeded the capacity of the rheometer. (Once the yield stress exceeds about 1,300 Pa, it can no longer be measured by the technique described here.) It is worth pointing out, however, that Vicat needle penetration is not a well-defined rheological parameter but rather an empirical measurement produced by a complex and ill-defined stress state, and probably the two measurements should not be expected to correlate.

Quite obviously, either rheological behavior or penetration can be used to probe setting of cement paste. The rheological measurements appear to be more sensitive. They are clearly more versatile. Yield stress can be measured for pastes with a wide range of w:c levels and at w:c levels more typical of mortar and concrete, whereas Vicat or Gillmore penetration requires a very low w:c. Either before or during yield stress measurement, one can subject the paste to shear that simulates any field conditions. Particularly important is the fact that the rheological measurements produce fundamental parameters, while penetration is an empirical measurement. Information from rheology will help us build scientific knowledge concerning the microstructure and its development during the early hydration period, especially during the induction period when few other techniques can be used successfully. Thus, rheological measurements offer several advantages over more traditional penetration tests for determination of setting time.

Conclusions

A number of conclusions have been drawn from this study:

1. Setting behavior of fresh cement paste has been successfully probed by rheological measurements. Creep/recovery measurements in which the applied stress is always less than the yield stress allow determination of yield stress without causing microstructural breakdown. The method

allows sequential measurements on a single specimen.
2. Yield stress increases slowly at first, then more rapidly. The rapid increase in yield stress occurs at the end of the induction period and corresponds to initial setting.
3. Paste with a lower w:c has a shorter initial setting time.

Acknowledgments

This research was supported by the National Science Foundation through the Center for Advanced Cement Based Materials and through a Young Investigator Award to the first author. We are grateful to Dr. Amnon Katz for help with the calorimetry measurements, and to Prof. C.F. Zukoski for helpful discussions on rheology.

References

1. Mindess, S.; Young, J.F. *Concrete;* Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1981; p 222.
2. Chen, Y.; Odler, I. *Cem. Concr. Res.* **1992,** *22,* 1130–1140.
3. Struble, L.J. In *Advances in Cementitious Materials;* Mindess, S., Ed.; Ceramic Transactions, 16; American Ceramic Society: Westerville, OH, 1991; pp 7–26.
4. Tattersall, G.H.; Banfill, P.F.G. *The Rheology of Fresh Concrete;* Pitman Advanced Publishing Program: London, 1983; p 278.
5. Struble, L.J., Schultz, M.A. *Cem. Concr. Res.* **1993,** *23,* 1369–1379.
6. Powers, T.C. *The Properties of Fresh Concrete;* John Wily & Sons: New York, 1968.
7. Helmuth, R.A. *Int. Congress Chem. Cement (ICCC) 7th 1980;* VI, 0/16–0/30.
8. Diamond, S. In *Advances in Cement Manufacture and Use;* Gartner, E., Ed.; Engineering Foundation: New York, 1989; pp 131–132.
9. Nguyen, Q.D.; Boger, D.V. *Annu. Rev. Fluid Mech.* **1992,** *24,* 47–88.
10. Min, B-H.; Erwin, L.; Jennings, H.M. In *Advances in Cementitious Materials;* Mindess, S., Ed.; Ceramic Transactions, 16, American Ceramic Society: Westerville, OH, 1991; pp 337–346.
11. Schultz, M.A.; Struble, L.J. *Cem. Concr. Res.* **1993,** *23,* 273–283.