ACI MATERIALS JOURNAL TECHNICAL PAPER

Title no. 104-M16

Cementitious Paste Setting Using Rheological and Pressure Measurements

by Sofiane Amziane and Chiara F. Ferraris

The measurement of the evolution of mechanical characteristics of concrete during the setting period is needed to control the schedule of construction (for example, placement and formwork removal). The standard Vicat test for measuring the setting time of cement paste and mortar does not provide sufficient information (initial and final set time), for example, to determine the time during which concrete can be pumped or extruded. This study monitored the cement paste setting period through the variation of intrinsic material parameters (yield stress and plastic viscosity) and the hydraulic pressure on the forms. The setting was monitored by rheological (stress growth and shear rate sweep) and hydraulic pressure measurements. The results of these experiments are discussed and compared with the Vicat test for cement paste. It is shown that the proposed tests are more sensitive to the setting evolution of cement paste than the Vicat test and provide useful early age information.

Keywords: cement paste; rheology; setting time; stress; yield.

INTRODUCTION

The monitoring of the evolution of mechanical, thermal, or physicochemical phenomena is the objective of the majority of the measurement methods for cement paste during the setting period. The first measurement methods for setting time were proposed in the 19th century.[1] The setting time was measured exclusively using mechanical methods based on the idea that stiffening during set induces a gradual increase in resistance to shearing of the cement paste. The first devices based on this principle imposed a local shear stress by the penetration of an object into the material. This concept is applied in the Vicat needle test. The Vicat needle is cylindrical, with a 1 mm^2 (0.0015 $in.^2$) cross section and moves in a vertical scaled guide, penetrating a mass of cement paste placed in a mold. Initial set is defined as the time at which the needle will not penetrate past a certain distance from the top of the sample (typically 25 mm [1 in.]). Final set is defined as the time when there will be no mark upon the surface from the needle, that is, no penetration of the needle at all. The Vicat needle is the test most used by present cement manufacturers to define setting time and is the subject of multiple standards (for example, ISO 9597[2] and ASTM C 191-04[3]) around the world. The concept of this test was also adapted for mortar and concrete by modifying the dimension of the needle (ASTM C 807[4] and ASTM C 403[5]).

Setting time measurements have also used other techniques, for example, one test is based on heat of hydration.[6] Methods of observation such as the scanning electron microscope (SEM) allowed a better understanding of the cement hydration and other related physical phenomena, leading to the emergence of numerous sophisticated methods, such as acoustic wave propagation,[7,8] electrical conductivity,[9] or the measurement of plastic shrinkage.[10] Despite the fact that today the phenomena of setting is known, the measurements obtained are not easily related to field conditions, as they are not directly related to mechanical phenomena such as stress and deformation.

Another method to measure the setting time of cement paste is based on the measurement of the hydraulic pressure variation at early age.[11] According to the Terzaghi principle, the stress in any point of a section through a particulate material can be computed from the total principal stress σ that acts at this point. If the voids in the material are filled with water under stress u, the total principal stress consists of two parts. One part acts on the water and on the solid surfaces in every direction with equal intensity. The balance $\sigma' = \sigma - u$ represents an excess over the hydraulic pressure u and is based exclusively in the solid phase of the material. This fraction of the total stress will be called the effective principal stress. Just after mixing, a cement paste is a suspension with a very high concentration of solid particles, composed of water, air, and cement. The paste, initially, is in a disorganized state. Solid particles are suspended in the liquid phase, which bears all forces applied to the system. In the plastic stage, it was found[12,13] that both σ and u are almost equal (that is, $\sigma' = 0$). The hydraulic pressure u is then equal to the total lateral pressure ($u = \rho g z$), where ρ is the density, g the gravitational constant, and z the height of the material. Thereafter, the development of the physical and chemical properties of the cement, which occurs within the first 3 to 4 hours after placing, induces a drop of the hydraulic pressure on the formwork, because the material becomes a solid that can sustain itself.

To measure the hydraulic pressure of cement paste, an original device presented in Reference 12 was adapted from the design of the triaxial setup usually used in soil mechanics. This method described herein has also been successfully used by Assaad and Khayat[13]and Assaad et al.,[14] leading to the same results. The method is very simple and capable of recording cement paste properties during the evolution of set before the Vicat test is able to detect any changes in the cement paste. It should be remembered that the Vicat needle method can only be used for cement paste or mortar, while the hydraulic pressure method can also be used for concrete as described in Reference 11. The hydraulic pressure becomes zero as the material stabilizes, that is, the lateral pressure against the formwork is equilibrated by the internal strength generated by the hydration process. This gives a potential indication of when it would be possible to remove the formwork. Obviously, other factors should be

ACI Materials Journal, V. 104, No. 2, March-April 2007.
MS No. M-2006-047.R1 received May 5, 2006, and reviewed under Institute publication policies. Copyright © 2007, American Concrete Institute. All rights reserved, including the making of copies unless permission is obtained from the copyright proprietors. Pertinent discussion including authors' closure, if any, will be published in the January-February 2008 *ACI Materials Journal* if the discussion is received by October 1, 2007.

ACI member **Sofiane Amziane** *is an Associate Professor of civil engineering at the University of South Brittany at Lorient, France. He is a member of ACI Committee 236, Material Science of Concrete. His research interests include the evaluation of concrete pressure against formwork, cement paste setting time measurement, and monitoring of rheological properties and hydraulic conductivity of cement paste during the setting period.*

Chiara F. Ferraris, *FACI, has been a physicist at the NIST Building and Fire Research Laboratory, Materials and Construction Research Division, since 1994. She is Chair of ACI Committee 238, Workability of Fresh Concrete, and Past Chair of ACI Committee 236, Material Science of Concrete. Her research interests include the rheology of cement paste, mortar, and concrete.*

considered before the forms are removed, such as the effects of vibration (due to banging to remove forms) on the concrete stability. A recent experiment, discussed in References 15 and 16, performed in the field with the hydraulic pressure method adapted for large formwork has demonstrated that the final zeroing of hydraulic pressure can be linked to successful formwork removal.

Another method of monitoring cement paste set can be based on the evolution of rheological measurements versus time.[17] The rheological behavior of a fluid such as cement paste, mortar, or concrete is often characterized by two parameters: yield stress τ_0 and plastic viscosity μ, as defined by the Bingham equation

$$\tau = \tau_0 + \mu\dot{\gamma} \tag{1}$$

where τ is the shear stress applied to the material (in Pa), τ_0 is the yield stress (in Pa), μ is the plastic viscosity (in Pa·s), and $\dot{\gamma}$ is the shear strain rate (also called the strain gradient) (in s^{-1}).

Several types of rotational rheometers exist[18,19] for measuring the Bingham parameters. The selection of a geometry for a rotational rheometer is usually based on several considerations, such as sedimentation, slippage, flow uniformity of the sheared material, and distance between the shearing planes.[20] A parallel plate configuration (refer to Fig. 1(b) and (c))[19] was used in this study. Typical rheological measurements are concentrated on the measurements of yield stress and plastic viscosity within a few minutes of mixing. Nevertheless, Ish-Shalom et al.[21] used a coaxial rotational rheometer with cement paste at various times after mixing and for a range of water-cement ratios (*w/c*) and showed that plastic viscosity and yield stress increase significantly during the setting period. This result may be explained by several closely connected physico-chemical and mechanical phenomena that occur when the water and cement are in contact.[22,23] The work described by Helmuth[24] shows that the stiffening of the cement paste is related to the interaction of the liquid and solid phases. Nonat et al.[25] explain that early hydration reactions of the cement affect the specific area, and free water content and, therefore, the water-film thickness around particles during the dormant period. The hydraulic pressure, as well as the rheological properties, depends on the water thickness because the water is the lubricant that keeps the particles separated. Therefore, the measurement of the variation of hydraulic pressure and variation of the rheological properties should help describe the evolution of setting.

Despite the long tradition of characterizing cement paste time evolution by the initial and final setting time, these values are not sufficient to answer some of the more practical questions related with constructability such as:

- What is the period during which the material is pumpable?
- What is the period during which the material has rheological properties allowing casting of the concrete without loss of future mechanical characteristics?
- When is it possible to remove the formwork?

The answer to these questions is of paramount importance for the civil engineer to design a concrete meeting a given construction schedule. To answer the above questions, however, the flow properties of the material need to be known.

RESEARCH SIGNIFICANCE

The measurement of the evolution of mechanical characteristics during the setting period of cementitious materials is necessary to control the schedule of structures construction (placement and time for formwork removal). To characterize setting of the cement paste, the Vicat test is often used. The information obtained (initial and final set), however, is largely insufficient. Monitoring the cement paste setting period through the changes in the intrinsic material parameters (yield stress and plastic viscosity), and the hydraulic pressure on the forms was investigated. All tests were conducted with cement paste. The results, however, are believed to be applicable to concrete because setting time is strongly influenced by the cement paste composition.

EXPERIMENTAL PROGRAM

Materials

The mixture compositions of the cement pastes (P30, P36, and P45) included in this experimental program are presented in Table 1. The main difference among these cement pastes is their *w/c*. The cement used (CEM II/B-LL-32.5 R) contains mass fractions of 70.5% clinker, 4.5% gypsum, 24% limestone, and 1% filler. The calculated Bogue composition of this cement (mass fractions) is deduced from the chemical characterization (Table 2). The specific Blaine surface is 395 m^2/kg (1928 ft^2/lb). The initial setting time of the cement was tested as described in the standard ISO 9597,[2] with a *w/c* of 0.28, cement density of 3050 kg/m^3 (0.11 lb/$in.^3$), and is 145 minutes.

Preparation of mixtures

The cement paste for the hydraulic pressure test was prepared in a 20 L (5.28 gal.) mixer according to the standard ISO 9597.[2] The cement paste for the rheological measurements was prepared using the methodology developed by the Portland Cement Association (PCA).[24] This methodology consists of a blender mixer with a capacity of 1 L (0.26 gal.) connected to a speed controller and to a temperature-controlled water bath. The speed controller allows the speed of the blades in the mixer to be held at a preset speed regardless of the load. The controlled temperature bath is set to 15 °C (59 °F) in this

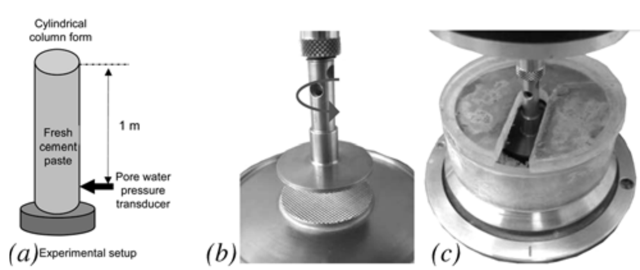

Fig. 1—Non-standard devices used for this study: (a) hydraulic pressure device; (b) serrated plate-plate rheometer; and (c) environmental control chamber.

study. This temperature allows the paste temperature to be approximately 20 to 22 °C (68 to 71.6 °F) to at the end of the mixing cycle. Without the temperature controller, the temperature of the cement paste would be much higher due to friction from mixing and this would affect the hydration of the paste as well as its rheological behavior. The cooled base of the mixer plays the role normally filled by the aggregates in concrete, which is that of a heat sink.

The mixing regime adopted for the cement paste was[19]:

- Add water to the mixer;
- The mixer blades rotate at a speed of approximately 419 rad/second (4000 rpm) while the cement is introduced in a period of 30 seconds;
- The speed of the blades is increased to 1047 rad/seconds (10,000 rpm) and kept constant for another 30 seconds;
- The mixer is stopped and the walls of the mixer scraped;
- After 2.5 minutes, the mixer is turned on again at a speed of 1047 rad/second (10,000 rpm) for 30 seconds; and
- The temperature is measured just after this cycle.

MEASUREMENTS

Setting measurement with Vicat needle

The Vicat device used is described in ASTM C 191-99.[3] The needle is on a 300 g (0.66 lb) moveable rod and has a diameter of 1 mm ± 0.05 mm (0.039 in. ± 0.0019 in.) A specimen of fresh cement paste is prepared and placed in a frustum 40 mm (1.57 in.) in height. Initial setting time is considered in this paper as the time when the needle penetration is 39 mm ± 0.5 mm (1.53 in. ± 0.019 in.) The final setting time corresponds to less than 0.5 mm (0.019 in.) penetration.

The Vicat measurements, as described in ASTM C191-99,[3] require that the cement paste be of normal consistency (ASTM C 187.[26] The scope of this study, however, is to determine the setting time of any cement paste. Obviously, the bleeding should be minimized by properly selecting the *w/c*.

Hydraulic pressure variations

A tubular glass column, measuring 1.3 m (51.2 in.) in height, 110 mm (4.33 in.) in diameter, and with a wall of 5.3 mm (0.21 in.) thickness, was used (Fig. 1(a)) as the container for the experimental material. Pressure measuring devices were positioned within the column 1 m (39.3 in.) below the top free surface of the cement paste.[12] The measured initial pressure was equivalent to the hydrostatic pressure. The reproducibility[12,20] (standard deviation calculated by repeating the test three times on the same material and under the same conditions) was found to be approximately ±5% when the pressure is positive, that is, before the pressure becomes zero, for all the cement pastes tested. However, a standard deviation of approximately ±15% of the value of the time at which the pressure reaches the lowest value (most negative) was recorded. It is possible that the hydraulic pressure measurements were affected by the uncontrollable small air bubbles observed in the devices at the end of each experiment. Other comparable experiments have shown the same phenomenon[13,14] of large scatter of the data for the negative peak.

Rheological properties measurements

A parallel-plate rheometer with 35 mm (1.38 in.) diameter serrated test plates (Fig. 1(b)) was used to measure the rheological properties for the cement paste. To limit as much as possible the evaporation/drying of the water during the test, the sample was enclosed in a chamber including a wet sponge (Fig. 1(c)). The mixing operation, described in the Preparation of Mixtures section, lasted 5 minutes, and another minute was needed to transfer the material from the mixer to the rheometer and to start the measurements. Therefore, the first test could only begin 6 minutes after the first contact of water with cement. Between rheological measurements, the mixture was stored in a hermetically sealed vacuum bottle. The test protocol includes the following:

- Except for the first test, which was conducted immediately after the initial mixing, the cement paste was homogenized before each test by the following method: the sides of the sealed vacuum bottle were scraped and the specimen was remixed for another 15 seconds using a blender plunged directly in the bottle. The remixing was performed to ensure that a representative sample was taken for the rheology test;
- 2 mL (0.07 oz) of fresh cement paste is transferred to the lower plate of the rheometer, using a disposable syringe (without the needle);
- The two plates were driven to the preset gap of 1 mm (0.039 in). This gap was selected based on previous experience[19,27]; and
- The test was carried out at a controlled temperature (23 °C ± 0.2 °C [73.4 °F ± 0.4 °F]), which is the average cement paste temperature during the setting period. The fresh cement paste is submitted to two types of shearing load: the stress growth test and the Bingham test.

The stress growth test is characterized by the material being sheared at a very low shear rate (0.1 s^{-1} herein). This shear rate was selected as the minimum shear rate possible with the available rheometer. The stress is recorded versus time for 5 minutes. The stress-time curve could be divided

Table 1—Cement paste composition

Mixture	Water, L/m^3 (gal./yd^3)	Cement, kg/m^3 (lb/yd^3)	*w/c*	ϕ_0	ρ, kg/m^3 (lb/in.^{3})
P30	478 (96.5)	1593 (2685.1)	0.30	0.52	2070 (0.075)
P36	523 (105.6)	1454 (2450.8)	0.36	0.48	1977 (0.071)
P45	579 (116.9)	1285 (2165.9)	0.45	0.42	1864 (0.067)

Note: ϕ_0 = solid volume fraction.

Table 2—Chemical characterization of cement by Bogue analysis

SiO_2	15.90%
Al_2O_3	3.90%
Fe_2O_3	2.15%
CaO	62.00%
MgO	0.80%
K_2O	0.80%
Na_2O	0.14%
SO_3	2.65%
C_3S	39.1%
C_2S	16.1%
C_3A	6.7%
C_4AF	6.5%

Note: Cement (CEM II/B-LL-32.5 R) used contains mass fractions of 70.5% clinker, 4.5% gypsum, 24% limestone, and 1% filler.

into three stages: 1) before the peak; 2) the peak; and 3) after the peak. The end of the linear behavior before the peak defines the real yield stress, but it is not possible to measure this point with the rheometer available due to the few points recorded before the peak value, especially at very early age (time <2 hours). The peak, defined by the maximum value, is easily measured and so is used as a good approximation of the yield stress.[28] A small error is introduced by selecting the peak itself instead of the end of the elastic period as a measure of the yield stress. A lower shear rate than the one used in this study would be desirable, because it would allow more stress measurements before the peak and therefore a more accurate determination of yield stress.

The Bingham test involves sweeping shear rates from 50 s^{-1} to 1 s^{-1}, and measuring the stress. The yield stress and the plastic viscosity as defined in Eq. (1) is determined by linear fit to the stress versus shear rate curve. After limited repeatability tests, it was found that the calculated values of the yield stress and plastic viscosity had a standard deviation of 5%.

RESULTS AND DISCUSSION

Hydraulic pressure variations during Vicat setting

The test results obtained by hydraulic pressure measurements are presented in Fig. 2. The hydraulic pressure decreases from hydrostatic pressure to zero, becomes negative, and then abruptly returns to zero.[12,29] This dip in pressure is called depression. As the *w/c* increased, the time to obtain a null pressure was delayed. One reason for the pressure decrease before the initial setting of the cement paste (Table 3), as defined by the Vicat test, is related to the relative humidity (RH) decrease due to the dissolution of alkaline hydroxides

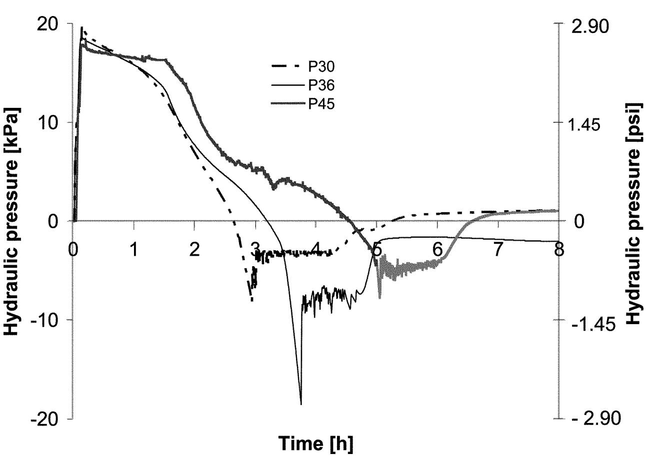

Fig. 2—Hydraulic pressure variation during hydration period. Value after P in the legend stands for w/c.

Table 3—Characteristic time obtained with different experimental devices*

Test	Rheometric test		Time to zero pressure	Vicat test	
Mixture	Time when yield stress gradient changed (pt B), hours	Time when viscosity became negative, hours	T_B, hours	Initial set, hours	Final set, hours
P30	3.13	1.6	2.49	2.50	4.28
P36	3.37	5.13	3.05	3.25	5.0
P45	5.83	6.75	4.07	4.01	6.16

*Uncertainties could not be calculated because these data are results of only one test.

from cement particles into the aqueous phase. The RH affects the level of the suction and thus produces the decrease of hydraulic pressure. Bentz et al.[30] demonstrated that the observed RH does not reach 100% because of the RH decrease caused by the dissolved ions (for example, Ca^{++} and Na^{+}) present in the cement paste pore solution. The RH initially recorded[30] stabilizes in the pore solution around 97% ± 2%. For example, according to Kelvin's law (Eq. (2)), a fall in RH of 2%, that is, 98% RH, involves a suction force of 2.8 MPa. Kelvin's law is given by

$$U_s = U_a - U_w = \sigma_{cap} = \frac{-\ln(\mathrm{RH})RT\rho_w}{gM} \quad (2)$$

where U_s is total suction, U_a is air pressure, U_w is water pressure, RH (%) is the relative humidity, M is the molar mass of water (M = 18.016 g × mol^{-1}), g is the acceleration due to gravity (g = 9.81 m × s^{-2} or 32.19 ft/s^2), R is the universal gas constant R = 8.3143 J × mol^{-1} × K^{-1}), T is the temperature in Kelvin, ρ_w the volumic mass of the water (Kg/m^3) and σ_{cap} is the capillary stress (Eq. (3)) or suction. For example, at 20 °C (68 °F)

$$\sigma_{cap} = \frac{-\ln(\mathrm{RH})RT\rho_w}{gM} = \frac{-10 \times \ln(0.98) \times 8.3143 \times (20+273) \times 1000}{9.81 \times 18.016 \times 10^{-3}} = 2.8 \text{ MPa (406 psi)} \quad (3)$$

These capillary forces; the gravity forces; attractive forces, such as Van der Waals forces; and electrostatic forces cause the solid cement particles to approach each other, so that the pore radii decreases. Simultaneously with the decrease of the water pressure during the setting period, some physical phenomena are induced, such as bleeding[31] and plastic shrinkage,[29,32] and rheological properties, such as thixotropy,[14,33] evolve. The magnitude of the σ_{cap} gives an indication of the total forces that are created to attract particles together from decreasing relative humidity. As they are very large, it is conceivable that they contribute significantly to the cohesiveness of the cement paste or concrete during setting.

When the cement paste is set, it is a solid and no longer behaves as a liquid that can exert a hydrostatic pressure. Therefore, the time corresponding to the pressure becoming null is proposed as a definition of the setting time of cementitious materials. This time can be determined by simple contact of the device test with the concrete.[16] It does not require rehandling the material, and it gives direct information on the mechanical evolution of the material. Additional discussion of the kinetics of the hydraulic pressure is given in Reference 14. This method can be used in cement paste, mortar, and concrete, while the Vicat needle test is only valid for cement paste or mortar.

Yield stress variation during setting period

The stress growth test is conducted to monitor the evolution of the yield stress with time.[34] Figure 3 shows a typical stress response obtained. It was noticed that the temperature of the mixture did not change significantly (less than 1 °C [33.8 °F]) during the whole duration of the tests. The times given to the right of the plot are the intervals after addition of water. The stress growth curve contains three stages: the pre-peak stage, the peak stage, and the post-peak stage.

In the pre-peak stage, the cement paste displays an elastic behavior as shown by the linear increase of the shear stress versus time at a constant shear rate. The cement paste is still acting as a solid, thus elastic behavior is observed. A nonlinear behavior follows, leading to the peak stress.

At early ages, the stress after the peak stress is reduced to an equilibrium value. At later ages (>4 hours), a stable equilibrium value is not reached, as shown by Fig. 3. The particles of cement are partially agglomerated at this point, and the layer of water between particles is reduced due to hydration. The shear action imposed by the rheometer can cause some of the agglomerates to break or overcome the solid-solid frictional forces. This may allow the paste to suddenly flow easily, leading to a reduction of the shear stress measured, followed by an increase as soon as the agglomerates or the friction prevents further flow.

Figure 4 shows the evolution of the yield stress (defined as the peak value) versus time for the three pastes studied. The key points to describe Figure 4 are Points A, B, and C. Point A is the initial yield stress, Point B is where the curve sharply increases, and Point C is the last measured point. For this study, Point B was selected as the last point before the sharp increase of the curve (Fig. 4). Usually Point C denotes the highest stress that was measurable for that material and for the test equipment used in this study. These points can be used for all curves in Fig. 4 to define two specific sections:

1. Section AB (from Point A to B): A slow steady increase of the yield stress with time; and

2. Section BC (from Point B to C): A dramatic increase of the yield stress, indicating the change of the cement paste from a fluid to a solid state.

A similar trend of the yield stress evolution as found by Struble and Lei[35] by using creep/recovery measurements on different cement pastes. The main difference between their method and ours is that Struble and Lei never sheared the cement paste above the yield stress; therefore, the cement paste microstructure never reached the point where the material flows.

It should be noted from Fig. 4 that P30 and P36 have the same setting time (as defined by the time to reach Point B). This is misleading, as there is only one data point between 2.5 and 3.5 hours after mixing for P36, whereas there are two points for P30. Therefore, the error to determine Point B is higher for P36 than for P30. In consequence, the difference of setting time of approximately 30 minutes observed with Vicat or pressure measurements is not observed with the yield growth method, because this difference is higher or equivalent to the estimated error in the measurement of B for P36. This indicates that measurements should be carried out every 15 minutes when using stress growth to determine setting time.

In Fig. 5, the slopes of Sections AB and BC from Fig. 4 were examined. For Section AB, the gradient decreases with increasing *w/c* (Fig. 4 and 5). In addition, the Point B appears earlier with decreasing *w/c* (Fig. 4 and Table 3). On the contrary, in Section BC, yield stress gradient increases with *w/c* (Fig. 5). These observations could be used to predict the influence of changes in cement paste composition on setting time without having to measure the cement paste behavior all the way until final setting time. Yield stress could be measured only for a set period of time and the gradient of Section AB calculated. A higher gradient in Section AB (Fig. 5) will indicate a qualitatively faster setting time without having to make quantitative measurements until Point B or C, as only a couple of points before Point B need to be used to calculate the slope. Further testing is needed to validate this claim and to establish the relationship between the gradient and setting time.

Figure 6 and Table 3 present, in different ways, the comparison of the various results obtained: yield stress, hydraulic pressure, and Vicat penetration. In Fig. 6, the hydraulic pressure, the yield stress, and the Vicat penetration value are represented as dimensionless ratios: the ratio of the hydraulic pressure (measured) to the hydrostatic pressure recorded initially, the ratio of yield stress to maximal yield stress, and the measured Vicat needle penetration divided by the measured penetration distance of 40 mm (1.57 in.), the

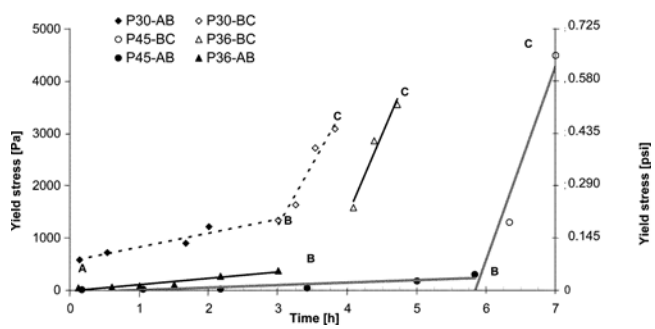

Fig. 4—Yield stress versus time during setting period for three cement pastes. Value after P in legend stands for w/c.

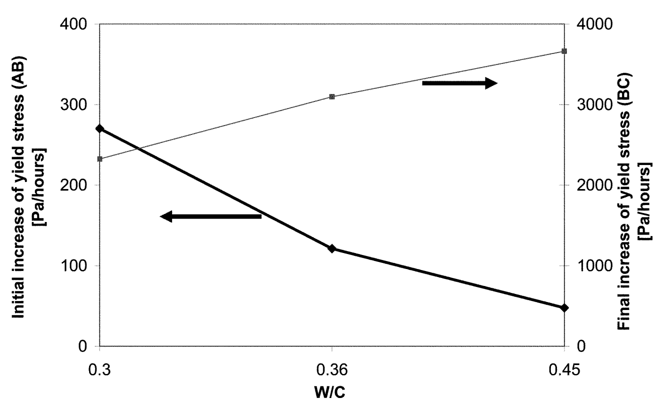

Fig. 5—Yield stress gradient comparison between [AB] and [BC] phase according to w/c. *Conversion factor: 1 Pa/h = 0.00015 psi/h (or 400 Pa/h = 0.06 psi/h).*

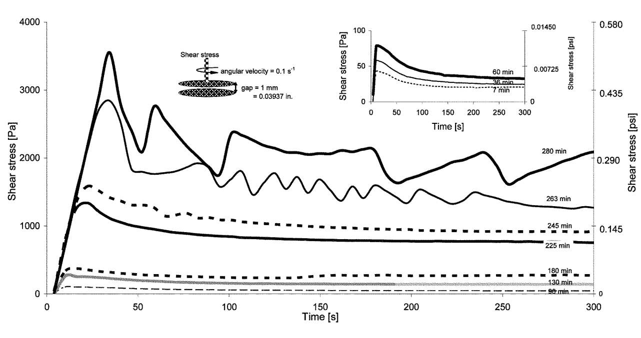

Fig. 3—Typical shear stress response obtained with stress growth experiment (P36 sample).

initial value. For the yield stress method, the time at Point B (Fig. 4) is defined as the setting time. From Table 3 and Fig. 6, it is clear that for all three types of measurements that the time obtained for setting times follow the same trend, that is, increasing with increasing *w/c*.

The two methods proposed, hydrostatic pressure and stress growth, could be used not only to determine setting time but also to monitor the process before initial set. This information could be used to better link material composition with concrete flow behavior.

Apparent viscosity during setting period

So far, the rheological study of the mixtures was limited to the yield stress as measured by stress growth. The most commonly used equation to describe concrete or cement paste flow is the Bingham equation as discussed in the Introduction. When performance is modeled using that equation, the slope of the shear stress-shear rate curve is determined and called the plastic viscosity, while the intercept is the yield stress. On the other hand, the non-Newtonian

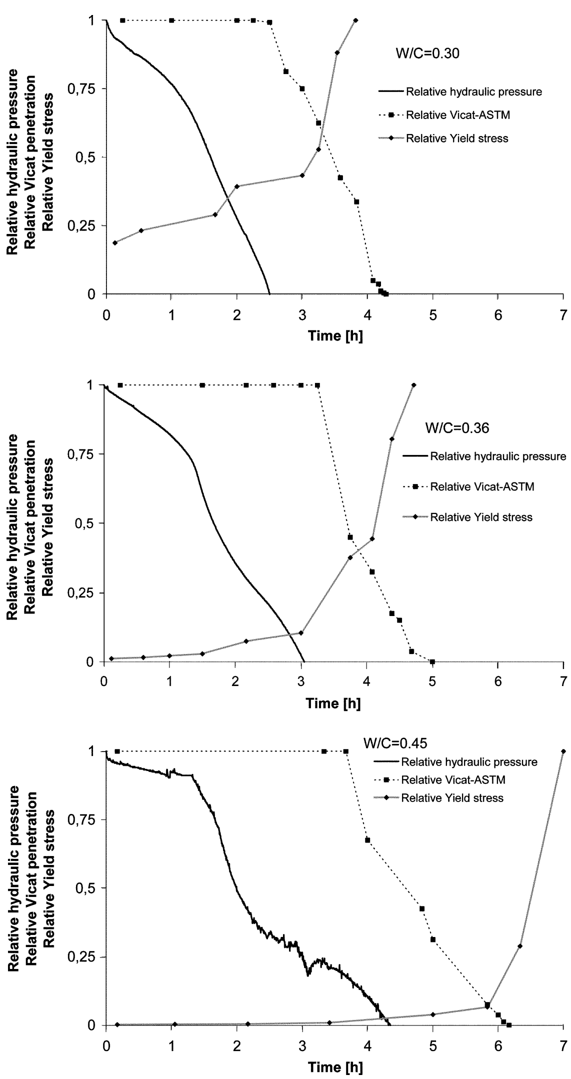

Fig. 6—Hydraulic pressures, yield stress, and needle penetration variation versus time according to w/c. *(Relative hydraulic pressure equals measured hydraulic pressure/hydrostatic pressure; relative Vicat penetration equals penetration of Vicat needle/40; relative yield stress equals measured yield stress/maximal yield stress measured.)*

viscosity is defined[36,37] as the ratio between the shear stress and the shear rate at any given shear rate. Flow curves are usually obtained by sweeping the shear rate from high to low values. In this study, the curves were recorded every 15 to 20 minutes for the P30 cement paste to determine the variation of viscosity and the yield stress during the setting period of the cement paste. All the shear stress versus shear rate curves are presented in Fig. 7. The slope and the yield stress (or intercept at zero shear rate) can be calculated from these curves and are discussed in the following.

First, the Bingham yield stress was calculated for each curve by taking the stress axis intercept of a linear fit to the curves shown in Fig. 7. The Bingham and the stress growth derived (copied from Fig. 4) yield stress are shown in Fig. 8. Both curves show the same trend. The yield stress calculated by Bingham, however, is systematically lower than that measured by stress growth. This is due to the shearing that occurs at the high shear rate applied to the cement paste during the Bingham protocol early in the test. For the stress growth test, the cement paste is not sheared at all before the measurement. In other words, the cement paste structure is destroyed before reaching the end of a Bingham test, whereas it is destroyed only after reaching the yield stress in the stress growth measurements.

The plastic viscosity defined by Bingham could be calculated from the slope of the shear stress-shear rate curve. From Fig. 7, however, it is obvious that the shear stress-shear rate curves are not linear. In certain cases, for low shear rate or 2 hours after mixing, a negative slope can be observed. It seems that there is dependence of the slope with the shear rate. Therefore, the slope of the curves of Fig. 7 was calculated using three consecutive points of the Bingham curve. The slope obtained was plotted at the shear rate of the middle value of three points selected (same principle as used to

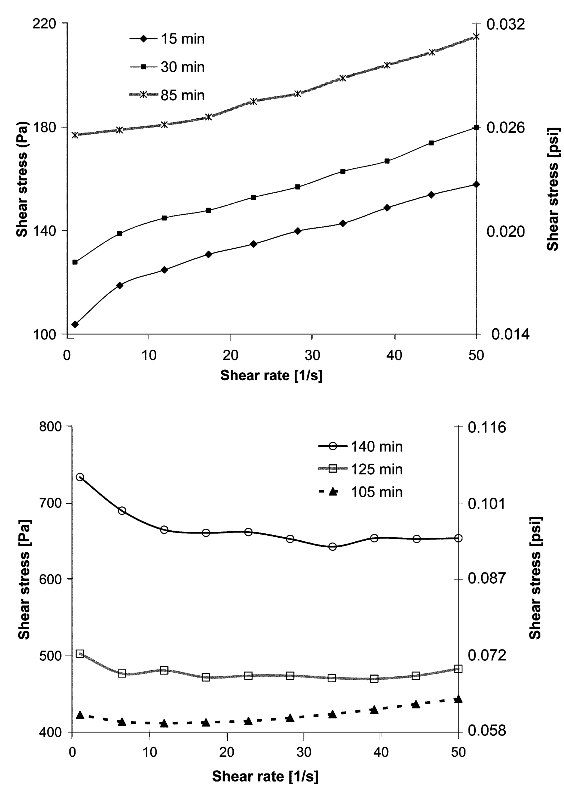

Fig. 7—Evolution of shear stress versus shear rate behavior during hydration period of P30 cement paste.

calculate moving average). The results are plotted in Fig. 9 and 10.

Just after mixing, the slope decreases as the shear rate increases (Fig. 9). This behavior is typical for a non-Newtonian material with a yield point.[37-39] After approximately 65 minutes, this tendency is reversed and the slope starts increasing with increasing shear rate. In other words, the shear stress increases when the shear rate decreases in a standard shear rate sweep (from high shear rate to low shear rate) used in the Bingham method. This transition could be interpreted as the transition to a zone where the frictional forces play a major role. As the hydration progresses, agglomerates form and, as less free water is present, the number of solid-solid contacts increases.[24] At a higher shear rate, however, these agglomerates can be broken and therefore the cement paste can flow, so that the shear stresses measured are relatively low. As the shear rate decreases, the agglomerates can reform, preventing free flow, so that the shear stress measured is higher. This behavior becomes even more apparent as time progresses, leading to a slope decreasing dramatically with time (Fig. 10) and even becoming negative. At high shear rates (above 25 s^{-1}), however, the slope is almost constant with time. This means that a high shear rate is able to break the structure of a cement paste even at times closer to the setting time.

Obviously, as the curves in Fig. 7 are not linear and even show a negative slope, the plastic viscosity cannot be calculated. On the other hand, the non-Newtonian viscosity and the ratio of the shear stress to shear rate at various shear rates and measurement times can always be calculated (refer to Fig. 11); and it is always positive. It clearly shows that the viscosity increases with time. This increase is more dramatic at low shear rates.

At this point, there are two sets of information related to the evolution of the rheological properties of the cement paste with stress above the yield stress: 1) the non-Newtonian viscosity (Fig. 11); and 2) the slope of the stress-shear rate curve as a function of shear rate (Fig. 9). In the first case, no clear transition can be observed that could point to the set time. In the second case, a clear transition is observed from a positive slope to a negative slope (Table 3).

To explain the dramatic slope change from positive to negative (refer to Fig. 9 or 10), the work by Ancey and Coussot,[38] who performed tests on a model fluid whose characteristics have some similarity with cement paste, could be used. The viscosity of the model fluid was approximately 0.96 Pa × s and glass particles were added at approximately 60% solids concentration. This is comparable to the cement

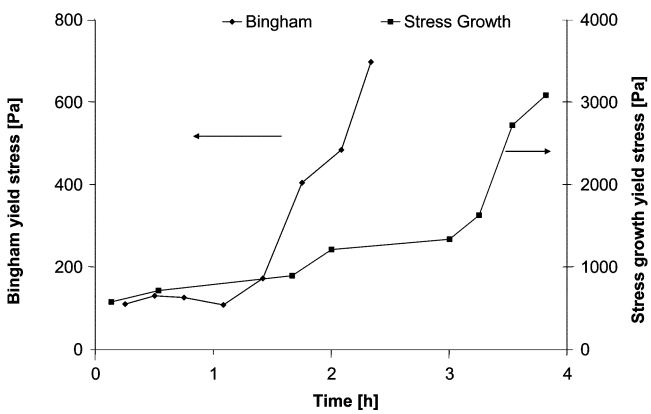

Fig. 8—Comparison of yield stress variation during setting period obtained with Bingham and stress growth methods for P30 cement paste. Conversion factor: 1 Pa = 0.00015 psi (or 800 Pa = 0.12 psi).

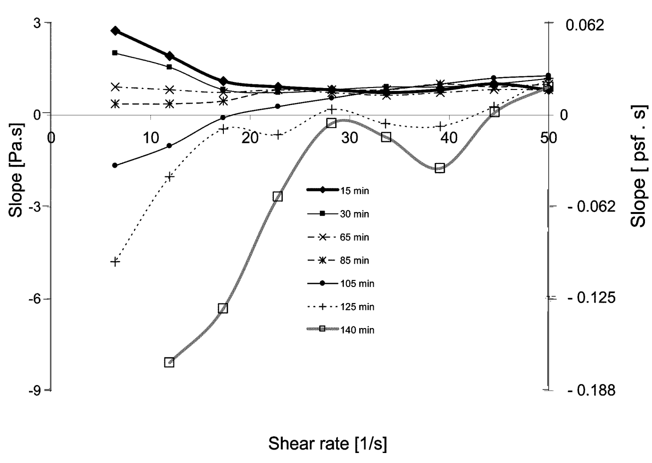

Fig. 9—Evolution of slope of shear stress-shear rate during hydration period of P30 cement paste (slope is obtained on every consecutive three points of Bingham curve and is plotted at shear rate of middle value of three points selected).

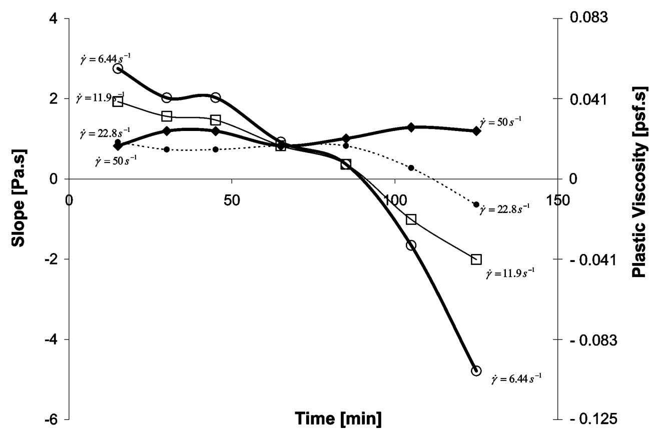

Fig. 10—Evolution of slope of shear rate-shear stress curve during hydration period (P30 cement paste). (Slope is obtained on every three points of Bingham curve, and shear rate is middle value of three points selected.)

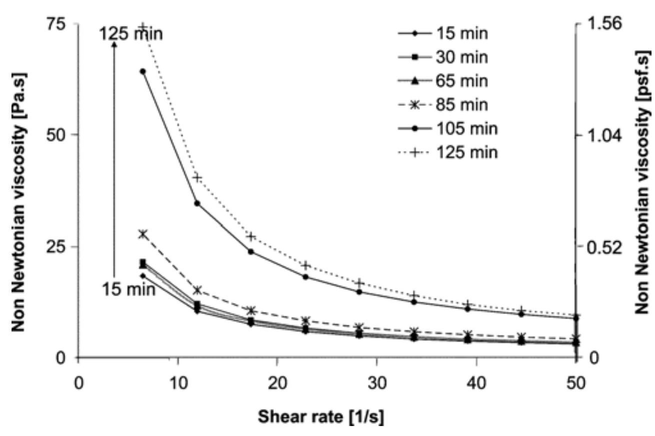

Fig. 11—Evolution of non-Newtonian viscosity during setting period (P30 cement paste).

paste specimens in this study where the solid concentration was 52% (Table 1) and the viscosity ranged between 0.9 Pa × s and 2.5 Pa × s (refer to Fig. 9) depending on the shear rate. Ancey and Coussot[40] explained that at low shear rates, frictional contacts between particles predominate. At larger shear rates, viscous forces are able to break direct contacts between particles and the medium forms a layer that provides lubrication. Once most contacts are lubricated, one may expect a viscous behavior at the macroscopic scale, as is usual for hard-sphere suspensions. To transfer these observations for an ideal fluid to the hydrating cement paste, it could be said that the cement paste behaves at early age as a low concentration suspension with lubrication provided by the free water. As the hydration progresses, the points of contact between the particles increase, and the free water available decreases, thus reducing the lubrication between particles provided by the water. As the cement paste is sheared at later ages, the high shear rate is still able to break the particle contacts, and as the shear rate is decreased, the contacts re-form, resulting in a high shear stress. Thus, the shear stress increases while the shear rate decreases, leading to a negative slope of the shear stress-shear rate curve (Fig. 10).

It could be deduced from these results that a suspension will not flow easily once the slope of the shear stress-shear rate curve shows a tendency to increase with shear rate. Could this be interpreted as the moment where the concrete is not pumpable? It is conceivable, although further tests need to be conducted to confirm this interpretation.

CONCLUSIONS

The focus of this paper was to examine the possibility of using alternative tests to the Vicat needle method to monitor setting time of cement pastes. It was shown that two other methods, the hydraulic pressure method and the rheology method described herein, are promising as they correlate well with the Vicat setting time and provide more information before the initial setting time than does the Vicat needle method.

The hydraulic pressure becomes null at the same time as when there is a change in the flow behavior of the material. This change in rheological behavior is seen by a strong increase in the yield stress and a sharp decrease of the slope of shear stress-shear rate curve (which becomes negative [Fig. 10]). This sharp change can be attributed to an increase in contact points between the particles due to hydration and the transformation of the material from a free-flowing fluid to a fluid with high frictional forces between the particles.

The appearance of negative slopes on the shear stress versus shear rate curve showed that the calculation of the plastic viscosity as described by the Bingham equation is not always applicable. In addition, the value of the non-Newtonian viscosity is strongly dependent on the shear rate applied and on the degree of hydration of the cement paste.

The methods proposed herein allow the monitoring of the evolution of the setting starting immediately from the mixing time, unlike the widely used Vicat measurement that shows no changes until initial set. It is conceivable that the Vicat method could be modified to detect changes in the cement paste before initial set, but such work is beyond the scope of this project. The practical applications of these methods can be easily imagined. Once the hydraulic pressure is zero, the concrete is not applying pressure to the formwork and it is self-supporting. It could be inferred that the formwork could be carefully removed with the concrete maintaining its shape. Therefore, the determination of the correct time for removal of the formwork could be done by monitoring the hydraulic pressure as an indicator of the evolution of the lateral pressure on the formwork.[14] Obviously, other considerations should be accounted for before the forms are removed, such as the effect of vibration (due to banging to remove forms) on the concrete stability. The initial gradient of the yield stress versus time, linked to the hydraulic pressure, could give an indication of the material performance. The evolution of the non-Newtonian viscosity is an indication of the flow capability of a material. The transition from a flowing material to a specimen governed by frictional forces, or almost solid, cannot be clearly determined by the change in viscosity. Further measurements should be performed to validate the applicability of this approach on concrete.

ACKNOWLEDGMENTS

The authors wish to thank N. R. Andriamanantsilavo and H. Bellegou for their contributions to the realization of the experimental program. The Région Bretagne and the VCCTL Consortium (NIST) should also be thanked for their financial contribution to this study. N. Martys, E. Garboczi, and D. Bentz of NIST and V. Picandet of the University of Lorient, France, are thanked for their useful comments.

REFERENCES

1. McKenna, C. F., "Hardness of Plasters and Cements, and a Simple Chronographic Apparatus for Recording Set," *The Journal of Industrial and Engineering Chemistry*, V. 70, No. 146, Feb. 1912, pp. 110-114.

2. ISO 9597, "Méthode d'Essai des Ciments—Détermination du Temps de Prise et de la Stabilité," P15-473PR et NF EN 193-3, *Ciment et Chaux*, Afnor, ed., 2003. (in French)

3. ASTM C 191-99, "Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle," ASTM International, West Conshohocken, Pa., 1999, 6 pp.

4. ASTM C 807-05, "Standard Test Method for Time of Setting of Hydraulic Cement Mortar by Modified Vicat Needle," ASTM International, West Conshohocken, Pa., 2005, 3 pp.

5. ASTM C 403/C 403M-06, "Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance," ASTM International, West Conshohocken, Pa., 2006, 7 pp.

6. Damasceni, A.; Dei, L.; Fratini, E.; Ridi, F.; Sow-Hsin, C.; and Baglioni, P., "A Novel Approach Based on Differential Scanning Calorimetry Applied to the Study of Tricalcium Silicate Hydration Kinetics," *Journal of Physical Chemistry B*, V. 106, 2002, pp. 11,572-11,578.

7. Carlson, J.; Nilsson, M.; Fernandez, E.; and Planell, J. A., "An Ultrasonic Pulse-Echo Technique for Monitoring the Setting of $CaSO_4$-Based Bone Cement," *Biomaterials*, V. 24, No. 1, 2003, pp. 71-77.

8. Boumiz, A.; Vernet, C.; and Tenoudji, F. C., "Mechanical Properties of Cement Pastes and Mortars at Early Ages," *Advanced Cement Based Materials*, V. 3, No. 3/4, 1996, pp. 94-106.

9. McCarter, W. J., and Curran, P. N., "The Electrical Response Characteristics of Setting Cement Paste," *Magazine of Concrete Research*, V. 36, No. 126, 1984, p. 42.

10. Boivin, S. G., "Retrait au Jeune Age du Béton: Développement dune Méthode Expérimentale et Contribution à l'Analyse Physique du Retrait Endogène," doctoral thesis, l'Ecole Nationale des Ponts et Chaussées, 1999, p. 251. (in French)

11. Amziane, S., "Setting Time Determination of Cementitious Material Based on Measurements of the Pore Water Pressure Variations," *Cement and Concrete Research*, V. 36, No. 2, 2006, pp. 295-304.

12. Andriamanantsilavo, N., and Amziane, S., "Maturation of Fresh Cement Paste within 1 to 10 m Large Formworks," *Cement and Concrete Research*, V. 34, No. 11, 2004, pp. 2141-2152.

13. Assaad, J., and Khayat, K. H., "Variations of Lateral and Pore Water Pressure of Self Consolidating Concrete at Early Age," *ACI Materials Journal*, V. 101, No. 4, July-Aug. 2004, pp. 310-317.

14. Assaad, J.; Khayat, K. H.; and Mesbah, H., "Variation of Formwork Pressure with Thixotropy of Self-Consolidating Concrete," *ACI Materials Journal*, V. 100, No. 1, Jan.-Feb. 2003, pp. 29-37.

15. Amziane, S., and Andriamanantsilavo, N., "Prediction of Cement Paste Pore Water Pressure Variations During Setting Period," *Advances in Cement Research*, Thomas Thelford, V. 16, No. 1, Jan. 2004, pp. 17-22.

16. Amziane, S., and Ferraris, C. F., "SCC Evolution of Formwork Hydraulic Pressure and Rheological Properties," *Workability of SCC: Roles of Its Constituents and Measurement Techniques*, SP-233, C. Shi and K. H.

Khayat, eds., American Concrete Institute, Farmington Hills, Mich., 2005, pp. 137-154.

17. Banfill, P. F. G., "The Rheology of Fresh Cement and Concrete—A Review," *Proceedings of the 11th International Cement Chemistry Congress*, V. 1, G. Grieve and G. Owens, eds., Durban, South Africa, 2003, pp. 50-62.

18. Tattersall, G. H., "Progress in Measurement of Workability by the Two-Point Test," *Properties of Fresh Concrete,* Proceedings of the Colloquium, RILEM, H.-J. Wierig, ed., Chapman and Hall, 1990, pp. 203-212.

19. Ferraris, C. F., "Measurement of the Rheological Properties of Cement Paste: A New Approach," *Role of Admixtures in High-Performance Concrete*, J. G. Cabrera and R. R. Rivera-Villarreal, eds., sponsored by Cementos Mexicanos, S.A. (CEMEX), March 21-26, 1999, Monterey, Mexico, RILEM Publications S.A.R.L., 1999, pp. 333-342.

20. Amziane, S., "Contribution à l'Etude des Matériaux Cimentaires à l'Etat Frais," thesis, Université de Bretagne Sud (France), 2005. (http://web.univ-ubs.fr/lg2m/labadmin/THESES/) (in French)

21. Nehdi, M., and Rahman, M.-A., "Estimating Rheological Properties of Cement Pastes Using Various Rheological Models for Different Test Geometry, Gap and Surface Friction," *Cement and Concrete Research*, V. 34, No. 11, 2004, pp. 1993-2007.

22. Ish-Shalom, M., and Greenberg, S. A., "The Rheology of Fresh Portland Cement Pastes," Fourth International of the Chemistry of Cement, 1960, pp. 731-749.

23. Kapranov, V. V., "Interaction of the Liquid and Solid Phases in the Process of Cement Hydration," *The VI International Congress on the Chemistry of Cement*, Moscow, Supplementary Paper, Section II, Sept. 1974, p. 12.

24. Helmuth, R. A., "Structure and Rheology of Fresh Cement Paste," *Proceedings of the Seventh International Congress on the Chemistry of Cement*, Paris, 1980, V. II, pp. VI 0-29.

25. Nonat, A.; Mutin, J. C.; and Jiang, S. P., "Physico-Chemical Parameters Determining Hydration and Particle Interactions During Setting of Silicate Cements," *Proceedings of the 10th International Congress of the Chemistry of Cement*, V. 2, (Cement and Hydration), ICCC, Göteborg, Sweden, 1997, pp. 2ii053.

26. ASTM C 187-04, "Standard Test Method for Normal Consistency of Hydraulic Cement," ASTM International, West Conshohocken, Pa., 2004, 3 pp.

27. Helmuth, R. A.; Hills, L. M.; Whitting, D. A.; and Bhattacharja, S., "Abnormal Concrete Performance in Presence of Admixtures," Portland Cement Association Serial No. 2006, 1995.

28. Nguyen, Q. D., and Boger, D. V., "Measuring the Flow Properties of Yield Stress Fluids," *Annual Review of Fluid Mechanics*, V. 24, 1992, pp. 47-88.

29. Radocea, A., "A Study on the Mechanism of Plastic Shrinkage of Cement-Based Materials," Publication P-92:9, Thesis no. 499, Göteborg, Sweden, 1992.

30. Bentz, D. P.; Jensen, O. M.; Hansen, K. K.; Olesen, J. F.; Stang, H.; and Haecker, C. J., "Influence of Cement Particle Size Distribution on Early Age Autogenous Strains and Stresses in Cement-Based Materials," *Journal of the American Ceramic Society*, V. 84, No. 1, 2001, pp. 129-135.

31. Josserand, L., "Ressuage des Bétons Hydrauliques," thèse de l'Ecole Nationale des Ponts et Chaussées, Oct. 2002. (in French)

32. Mounanga, P., "Etude Expérimentale du Comportement de Pâtes de Ciment au Très Jeune Age: Hydratation, Retraits, Propriétés Thermophysiques," thèse de Doctorat de l'Université de Nantes, Dec. 2003. (in French)

33. Assaad, J.; Khayat, K. H.; and Mesbah, H., "Assessment of Thixotropy of Flowable and Self-Consolidating Concrete," *ACI Materials Journal*, V. 100, No. 2, Mar.-Apr. 2003, pp. 99-107.

34. Ferraris, C. F., and Gaidis, J. M., "The Connection Between the Rheology of Concrete and the Rheology of Cement Paste," *ACI Materials Journal*, V. 88, No. 4, July-Aug. 1992, pp. 388-393.

35. Struble, L., and Lei, W.-G., "Rheological Changes Associated with Setting of Cement Paste," *Advanced Cement Based Material*, V. 2, 1995, pp. 224-230.

36. Hackley, V. A., and Ferraris, C. F., "The Use of Nomenclature in Dispersion Science and Technology," NIST Recommended Practice Guide, SP 960-3, 2001.

37. Schramm, G., *A Practical Approach to Rheology and Rheometry*, Haake, Karlsruhe, Germany, 1994.

38. Lootens, D.; Hebraud, P.; Lecolier, E.; and Van Damne, H., "Gelation, Shear-Thinning and Shear-Thickening in Cement Slurries," *Oil and Gaz, Science and Technologie—Revue de I'IFP*, V. 59, No. 1, 2004, pp. 31-40.

39. Struble, L., and Sun, G.-K., "Viscosity of Portland Cement Paste as a Function of Concentration," *Advanced Cement Based Material*, V. 2, 1995, pp. 62-69.

40. Ancey, C., and Coussot, C. R., "Transition from Frictional to Viscous Regime for Granular Suspensions," Comptes Rendus de l'Académie des Sciences, V. 327, Serie ii b, Paris, 1999, pp. 515-522.