A contribution from ACI Committee 236

Detecting the Fluid-to-Solid Transition in Cement Pastes

Comparing experimental and numerical techniques

BY GAURAV SANT, MUKUL DEHADRAI, DALE BENTZ, PIETRO LURA, CHIARA F. FERRARIS, JEFFREY W. BULLARD, AND JASON WEISS

The time of set for concrete is extremely important when scheduling construction operations. The fluid-to-solid transition that occurs during setting is crucial in assessing practical construction operations, such as finishing, sawcutting, and curing, and determining when test procedures such as early-age shrinkage measurements should be initiated.

The solidification of cementitious mixtures can be identified using a variety of techniques. Each of the investigated techniques indicates that solidification occurs after a similar time period and contributes to a more detailed understanding of the fluid-to-solid transition. The interpretation of the results of each technique are described from a fundamental viewpoint, along with additional insight into the behavior of concrete that the techniques help explain or illustrate. Details of the investigated test methods can be found in a companion paper[1] available with the online version of this article at **www.concreteinternational.com**.

TECHNIQUES SENSITIVE TO VOLUME CHANGE

The total volume reduction that occurs when cement and water react is described as the chemical shrinkage.[2] The reduction in external volume under sealed, isothermal conditions is described as the autogenous shrinkage. One method proposed to identify the fluid-to-solid transition is the deviation between chemical and autogenous shrinkage.[2-5] An illustration of this approach is provided in Fig. 1 for two paste mixtures containing portland cement and water with a water-cement ratio (w/c) = 0.30. One mixture (labeled w/c = 0.30WRA) contained a polycarboxylate-based high-range water-reducing admixture (HRWRA). The other mixture (labeled w/c = 0.30) did not contain any admixtures. At early ages, while the paste is fluid, it's unable to support stress as shrinkage occurs. As such, the cement paste collapses onto itself preventing the formation of internal vapor spaces. As a result, chemical and autogenous shrinkages are similar. As the system hydrates and a solid structure develops, however, the material is able to resist stresses, and the reduction in total volume (chemical shrinkage) begins to exceed the reduction in external volume (autogenous shrinkage) due to formation of vapor spaces in the system, commonly called self-desiccation. At this point, the chemical and autogenous shrinkage curves diverge.[2-6] The times of solidification were identified using this method to be 4.3 hours for w/c = 0.30 and 7.0 hours for w/c = 0.30WRA.

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The list of references and a companion paper containing details of the test methods discussed are available with the online version of this article at www.concreteinternational.com.

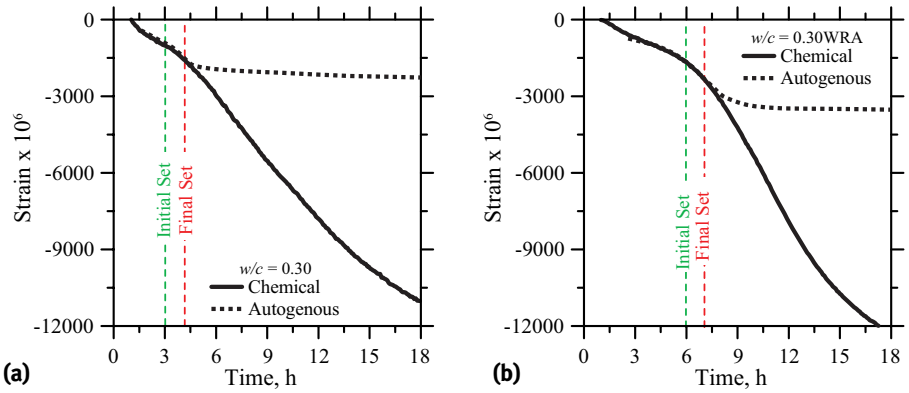

Fig. 1: The deviation of the total (chemical) and external (autogenous) volume change measurements used to identify solidification: (a) plain cement mixture (*w/c* = 0.30); and (b) mixture containing a polycarboxylate-based high-range water-reducing admixture (*w/c* = 0.30WRA). Initial and final set values determined from Vicat tests

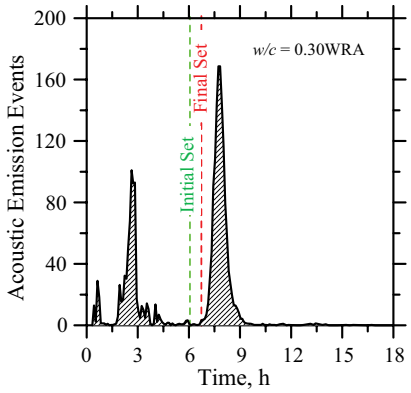

Fig. 2: The increase in acoustic emission events caused by the formation of vapor cavities is an indication of solidification in a sealed paste mixture (shown for *w/c* = 0.30WRA). Initial and final set values determined from Vicat tests

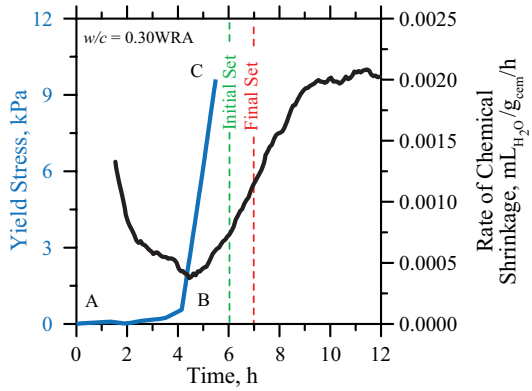

Fig. 3: Increase in yield stress identified by rheological property measurements of a hydrating cement paste (*w/c* = 0.30WRA). Initial and final set values determined from Vicat tests (1 kPa = 0.145 psi, 1 $mL_{H_2O}/g_{cem}/h$ = 1 $lb_{H_2O}/lb_{cem}/h$)

In concrete construction, the development of these vapor spaces promotes the suction of surface water into the concrete. This is commonly observed as the absorption of bleed water from a slab surface, which is an indicator often used to signal that the slab is beginning to set and is nearly ready for finishing operations to begin.

An alternative method that has been proposed to detect vapor-filled spaces is acoustic emission measurement. The response of cement paste *w/c* = 0.30WRA is shown in Fig. 2. After an initial period of low acoustic activity, a dramatic increase in acoustic events occurs at an age of 7 hours. The initial period of acoustic activity is not significant in that it corresponds to end of settlement of the cement paste in some mixtures and is characterized with low-energy acoustic events. The increase in acoustic activity that initiates at 7 hours agrees with the time of solidification assessed using the divergence of the volume change response (Fig. 1).[7] This increase in acoustic activity can be explained by the formation of vapor spaces when the chemical shrinkage and autogenous strain curves diverge. Consequently, the dramatic increase signals the formation of a load-resisting solid skeleton.[7] This acoustic activity decreases after a few hours, as it is believed that the vapor-filled spaces are expanding at this time (which would not correspond with acoustic activity) as opposed to forming new spaces.

TECHNIQUES SENSITIVE TO STRESS RESISTANCE OR DEVELOPMENT

For cement pastes, the most common technique used to identify set (initial or final), is the Vicat test that relates decreasing penetration of a needle under a constant applied load to the formation of a structure in the material. Another technique that may be used to study early-age behavior is rheological testing, which relates deformation under an applied shear stress to the development of a solid structure in the material. The development of a solid network can also be related to the ability of the material to generate a stress, identified using the ring test.[1]

Figure 3 shows the evolution of yield stress assessed by rheological testing, the rate of chemical shrinkage, and Vicat test setting times. The yield stress is seen to dramatically increase at Point B prior to the Vicat test set time. This corresponds more closely, however, to the end of the dormant period in cement hydration, when the rate of cement hydration (chemical shrinkage) begins to increase.[8] This observation is consistent with increasing hydration that results in decreasing interparticle distances and strengthening interparticle bonds, causing the measured yield stress to increase before the material solidifies.[8]

The traditional interpretation of initial and final set using the Vicat test are penetration depths of 25 and 0 mm (1 and 0 in.), respectively. At these penetration depths, the material has a shear resistance of

about 20 and 32 kPa (2.9 and 4.6 psi), respectively.[8] Consequently, the Vicat test is unable to detect material property development until the shear resistance of the material is at least 20 kPa (2.9 psi), which is higher than the values in Fig. 3 measured using the rheology test.[8]

The ability to identify solidification using residual stress development can be demonstrated using the restrained ring test. In this test, a ring of paste is restrained against shrinkage by an inner and outer ring instrumented with strain gauges. Stress and strain can only initiate in the system when the material possesses an elastic modulus, which is indicative of structure formation.[6,9] Consequently, the development of residual stress (or restrained strain) indicates the existence of a solid skeleton in the system. The development of restrained strain initiates at about 8 hours, as shown in Fig. 4, for paste mixture w/c = 0.30WRA.

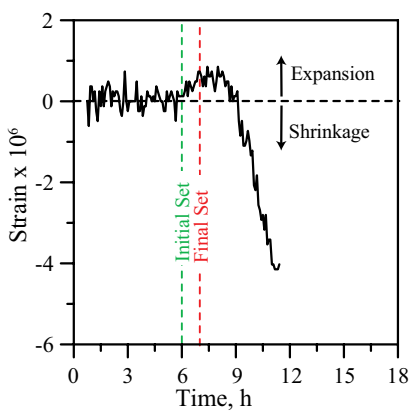

Fig. 4: Restrained shrinkage strain in a sealed hydrating cement paste (w/c = 0.30WRA) assessed using the dual ring test. Initial and final set values determined from Vicat tests

TECHNIQUES SENSITIVE TO STRUCTURE DEVELOPMENT

Ultrasonic testing has been extensively used to assess the time that it takes a high-frequency pulse to propagate through a cementitious sample.[10-12] The velocity of the ultrasonic pulse increases as the cementitious material hydrates (Fig. 5). Initially, when the cement paste is a suspension of cement particles in water, the preferential propagation medium is water (in de-aired pastes). When a skeleton develops, however, the pulse velocity begins to increase as the solid hydrates form an interconnected network that preferentially propagates the ultrasonic pulse.[13-15] The increase in velocity corresponds with the time of initial set as assessed by the Vicat test. This increase in the ultrasonic velocity also corresponds to the development of elastic properties in the solid material such as bulk and shear moduli. It should be noted that, in plastic pastes that are not de-aired, the preferential propagation medium is air. In these cases, the transmission velocity at early ages corresponds to the velocity of sound in air of about 340 m/s (1100 ft/s), as shown in Fig. 5(b).[13] After a solid structure has developed, the transmission velocities in the pastes are similar whether or not they have been de-aired. In systems with and without air, set occurs when the longitudinal velocity is greater than a value of about 1500 m/s (4900 ft/s) (the velocity of sound in water).

Results of numerical hydration modeling performed using the National Institute of Standards and Technology's CEMHYD3D can be used to provide "virtual" information of the progress on hydration and the development of solid hydrates in a cementitious material. As hydration progresses, an increase in the fraction of solids connected by hydration products can be used to identify the fluid-to-solid transition. CEMHYD3D identifies cement particles connected by hydration products and differentiates these hydrate connections from those that may result from simple initial cement particle contacts. As seen in Fig. 5(a), the results indicate a dramatic increase in the fraction of connected solids at the same time that the ultrasonic wave velocity is noted to increase, namely at 3 hours. It is important to indicate that the kinetic factor of the model that allows translation of model cycles to real time was calibrated using experimental measurements of chemical shrinkage performed on the plain cement mixture (w/c = 0.30). These results correlate solids forming in three dimensions to the

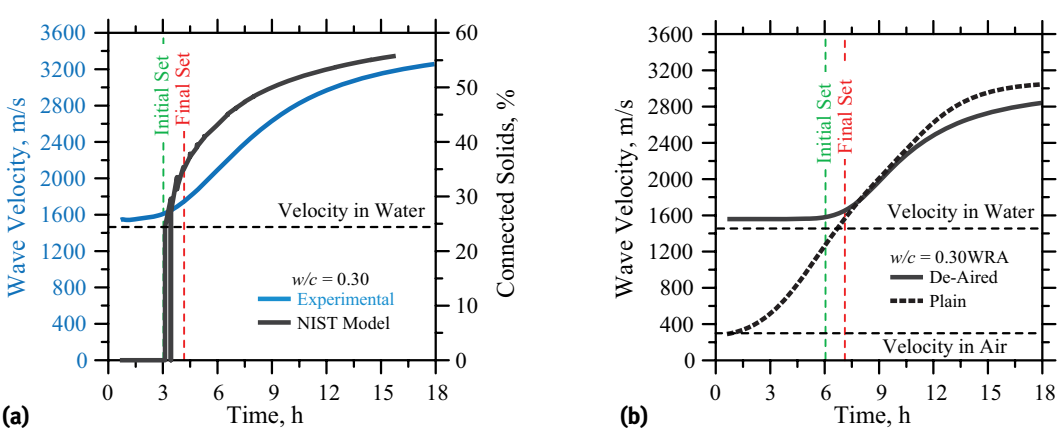

Fig. 5: Ultrasonic wave velocity as a function of time: (a) comparison with connected solids content for a de-aired plain cement paste mixture (w/c = 0.30); and (b) comparison of a de-aired paste mixture and a paste mixture containing dissolved air (w/c = 0.30WRA). Initial and final set values determined from Vicat tests (1 m/s = 3.28 ft/s)

development of a solid structure in the system as assessed by wave velocity measurements.

Another method of determining set time uses the modified parallel law to model the electrical response of cementitious materials[16,17]

$$\sigma_t = \sigma_0 \phi \beta \quad (1)$$

where σ_t is the conductivity of the bulk paste, σ_0 is the conductivity of the pore solution, ϕ is the volume fraction of the liquid-filled pores (capillary and gel pores), and β is the connectivity of the pore fluid. As the cement paste hydrates and water in the system is consumed, the volume of the pore fluid (ϕ) continuously decreases. The pore solution conductivity (σ_0) increases, as the consumption of water due to hydration increases the electrolyte concentration, and the ionic strength of the solution increases due to the release of potassium and sodium ions from the cement clinker phases. Further, electrical conduction pathways become more tortuous due to the formation of connected solid phases and the formation of vapor spaces. During self-desiccation, the largest remaining water-filled pores will empty first. Consequently, the change in tortuosity can be quite dramatic, which decreases the pore solution connectivity (β).[16] Because changes in pore solution conductivity and liquid volume act in opposite directions and tend to counterbalance each other at early ages, the change in pore solution connectivity (β) has been found to be the most significant.[17,18]

Figure 6(a) shows the electrical conductivity of a plain cement paste (w/c = 0.30) as a function of specimen age. After showing a small increase over the first 1.5 hours, paste conductivity decreases an order of magnitude during the time the test was performed. The rate of electrical conductivity change has previously been used to identify solidification in cementitious materials.[17,18] The

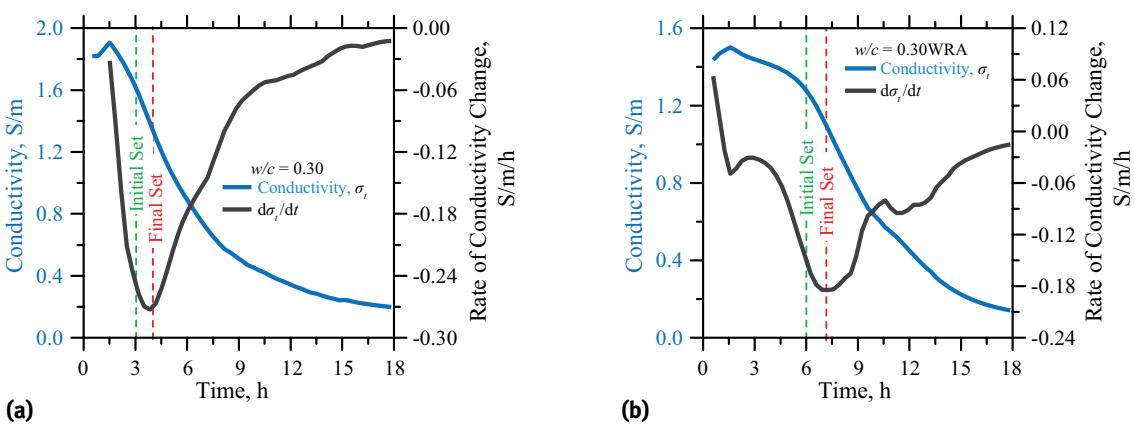

Fig. 6: Electrical conductivity and the rate of conductivity change ($d\sigma_t/dt$) for a sealed hydrating paste: (a) plain cement mixture (w/c = 0.30); and (b) mixture containing a HRWRA (w/c = 0.30WRA). Initial and final set values determined from Vicat tests

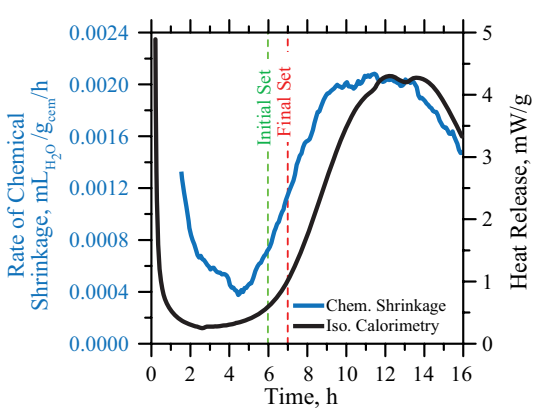

Fig. 7: The rate of chemical shrinkage and the isothermal heat release as a function of specimen age for a cement paste containing a HRWRA (w/c = 0.30WRA). Initial and final set values determined from Vicat tests (1 $mL_{H_2O}/g_{cem}/h$ = 1 $lb_{H_2O}/lb_{cem}/h$)

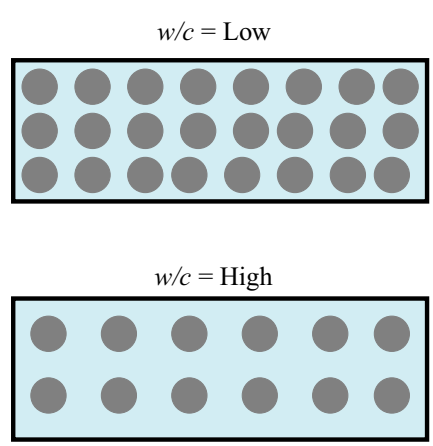

Fig. 8: An illustration of cement systems having varying (low and high) w/c

maximum rate of electrical conductivity change correlates well with the time of solidification as measured by other techniques (Fig. 6). This corresponds to a decrease in moisture connectivity (and conductivity) as the system gradually changes from a fluid to a solid. This is related to the development of a solid structure and the formation of vapor spaces in the system. A similar response is observed for both paste mixtures investigated.

RELATING STRUCTURE DEVELOPMENT TO DEGREE OF REACTION

An important consideration in assessing the fluid-to-solid transition in cementitious materials is to identify a distinction between the degree of reaction experienced by the system and the development of a solid structure. The rates of chemical shrinkage and isothermal heat release have been extensively used to identify the rate at which the hydration reaction is progressing.[6,19-22] Equivalency between these two measures has been demonstrated in several past studies.[19,23,24] For the *w/c* = 0.30WRA paste, the rates of heat release and chemical shrinkage are shown in Fig. 7. Several studies have attempted to correlate solidification and the rate of heat release.[25,26] From a fundamental viewpoint, however, solidification should not be related to the rate of reaction, but rather to the development of a solid structure.[27] This conclusion is justified by rheological evaluations of cement systems that have correlated the increase in the yield stress to an increase in the rate of heat release and chemical shrinkage.[8,28] In these experiments, it was observed that the time the yield stress begins to increase does not correlate to solids formation, but rather corresponds to an increase in the rate of hydration.[6,28]

The early-age physical development of a solid network depends on the particle size (cement fineness), *w/c*, and the solid-to-solid spacing in the system (flocculation versus dispersion). This is illustrated by the simple example in Fig. 8, showing two systems having different *w/c*. These systems have significantly different initial solid-to-solid spacing. The extent of structure development (and reaction) needed to develop the solid structure is obviously greater in the case with a high *w/c* and larger interparticle distances. Consequently, low *w/c* systems (with smaller interparticle spacing) would need a smaller volume of hydration products and a smaller extent of reaction to form a solid network capable of resisting a stress. This can be extended to the case of the two mixtures evaluated in this article, a dispersed system containing an HRWRA and a flocculated system with no HRWRA, that have equal volume fractions of cement and solution.

These considerations show that it is incorrect and inappropriate to relate solidification to a single discrete value of the degree of reaction experienced by the material. To further support the inherent difficulty in using chemical shrinkage or isothermal calorimetry alone to assess setting, it's noted that the Vicat time of setting may vary by several hours as *w/c* is increased from 0.30 to 0.45, but the isothermal calorimetry heat of hydration and chemical shrinkage curves obtained for cement pastes within this range of *w/c* may be nearly identical to one another.[29-31]

It must also be recognized, however, that most cement-based materials with *w/c* in the range of 0.30 to 0.50 will set soon after the end of the dormant period. Because the increase

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in hydration rate at the end of the dormant period is so dramatic, sufficient hydration to achieve setting (for this range of w/c and typically encountered cement finenesses) will occur in just a few hours. This helps explain how, in engineering practice, calorimetric measurements are used to estimate physical setting times, while from a materials science perspective, heat generation and setting time are not directly related.

SUMMARY AND CONCLUSIONS

Although each of the assessment techniques discussed in this article probes a different material response, solidification is identified within a similar time interval. Tests that assess volume change and the creation of vapor spaces correspond well with the development of solids and the development of a stress-resisting network. Techniques such as calorimetry, rheology, and chemical shrinkage show a more gradual increase over time because they are related to the hydration reaction that accelerates before the time that the fluid-to-solid transition occurs.

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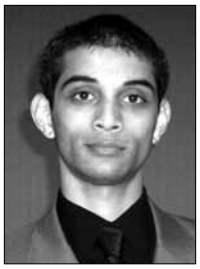

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Detecting the Fluid-to-Solid Transition in Cement Pastes: Assessment Techniques

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Abstract

The setting time of concrete is essential for scheduling construction operations. The fluid to solid transition that occurs during setting is crucial in assessing practical construction operations such as finishing, saw-cutting, and curing. The fluid to solid transition also indicates the time when test procedures should be initiated, such as early-age shrinkage measurements. Traditionally, this transition has been insufficiently related to material science concepts, instead being conventionally identified by empirical test procedures such as the Vicat test or the Penetration test (ASTM C191 and C403). While empirical tests are beneficial for practical applications and quality control processes, these procedures are not capable of relating a change in penetration resistance to a specific aspect of structural evolution in the material, the degree of reaction, or residual stress development. This paper is the first of two parts that describes a variety of techniques that are capable of identifying and quantitatively characterizing the fluid to solid transition in cement pastes. This paper provides a description of the fundamental concepts behind each assessment technique. A companion paper will compare their results.

Keywords: *Solidification, early-age, setting, degree of reaction, stress development, Vicat test*

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1. Introduction and Background

Setting (or solidification as it will be designated in this series of papers) describes the transition that a cement paste experiences as it is transformed from a fluid to a solid[1]. Setting in cement pastes and the sieved mortar fractions of concrete has been traditionally identified using penetration resistance techniques (ASTM C191 and C403). While these empirical tests have practical significance, the distinction between empirical measures (such as the Vicat test) and tests that assess a fundamental change in the material's structure is important. New techniques to assess solidification in cement paste, mortar or concrete should identify how they are related to the fundamental response of the system. For example, researchers[2,3] have shown that shrinkage experienced by the system (especially for systems having a low water-solid mass ratio (*w/cm*)) should be assessed from the time of solidification. This is because volume changes experienced by the system while it is fluid are less significant in leading to residual stress development and early-age shrinkage cracking[4,5]. This highlights the need for the development of experimental assessment techniques that are capable of identifying solidification in the most fundamental way. In this paper, the authors describe a variety of techniques capable of assessing the fluid to solid transition in cement systems. These techniques are summarized in Table 1. A companion paper compares the time of solidification as identified using each of these techniques and their interpretation to determine the timing of the fluid-to-solid transition.

2. Research Significance

Researchers have used a variety of techniques to assess the solidification process in cement-based materials including ultrasonic wave velocity[6,7,8], volume change[2,9], electrical conductivity[10,11], hydraulic pressure variation[12] and rheological measurements[13]. However, comprehensive studies that directly compare these test-methods for identical paste, mortar or concrete systems are not common[14,15]. While this series of papers examines solidification using a variety of experimental (volume change, electrical, acoustic emission, ultrasonic pulse propagation, restrained ring tests, and isothermal calorimetry) and numerical modeling (CEMHYD3D) techniques using the same cement paste system, it should be noted other

techniques not discussed here can also be used to identify solidification. A review of other alternative and complementary techniques can be found elsewhere[14,15]. In this first paper in the series, the authors present the fundamental principles and experimental procedures on which these techniques are based[5,16,17,18,31,42,47].

3. Experimental Procedures

A. Chemical Shrinkage Measurements – Buoyancy Method Protocol

The volume of hydrated (reacted) cement paste is smaller than the initial volume of solids and water. This reduction in volume is known as chemical shrinkage[19,20,23]. Chemical shrinkage can be assessed as a volume reduction by measuring the amount of water imbibed by a hydrating paste specimen as a function of time. Chemical shrinkage is useful for assessing the rate and extent of hydration of cement pastes at early ages and for determining the quantity of water needed to internally cure the mixture[21,22]. A standard test method, ASTM C1608, is available for assessing chemical shrinkage and automated procedures for assessing chemical shrinkage have also been proposed[16,16,20].

For this study, chemical shrinkage was measured using an automated technique based on the buoyancy protocol[16] for a 25 g paste specimen with 10 g of surface water. An illustration of the experimental setup is shown in Figure 1; in this test a paste sample in a crystallization dish was suspended from a balance plate in paraffin oil. The change in mass was used to determine the chemical shrinkage and ultimately the degree of hydration (DOH) of the paste, considering an assumed ultimate value of 0.064 ml of chemical shrinkage per gram of cement when completely reacted[23].The test is sensitive to the presence of air, which would influence the imbibition of water into the sample. At later ages, especially in specimens with low *w/cm*, the test is sensitive to the specimen thickness, since water may not penetrate the system rapidly enough to keep up with ongoing hydration[16,20].

B. Autogenous Strain Measurements – Membrane Method Protocol

Autogenous strain is a term used to describe the external volume change experienced by a hydrating system when the system is sealed and does not experience a change in temperature[23]. Autogenous strain is driven by chemical shrinkage and is similar to chemical shrinkage when the paste is fluid (before solidification). The fluid system does not allow for the creation of empty porosity and the chemical shrinkage results in an equivalent external volume change as the system collapses. After solidification, however, the paste cannot collapse freely and vapor spaces are cavitated. These voids, if small enough, as in the case of low *w/c*m systems, can generate substantial capillary pressures and shrinkage. A standard for measuring autogenous strain at early age does not currently exist, but a draft procedure has been proposed (ASTM Sub-Committee 09.68) to standardize measurement of autogenous deformation for cement pastes and mortars using the corrugated tube protocol[16,24].

While the corrugated tube is easier to implement for measurements performed after set, in this study, autogenous strain was assessed using the membrane method protocol[16], which involved

encapsulation of the fresh paste in a polyurethane membrane. The membrane was then suspended from a balance plate in a paraffin bath[16]. An illustration is provided in Figure 2. It should be noted as chemical shrinkage and autogenous strain are similar prior to set, but diverge after solidification. Therefore, the point of divergence of these measurements can be used to identify set[16,25]. Techniques for the assessment of autogenous strain are restricted to systems that are insensitive to bleeding as the reabsorption of bleed water by the sample provides a false indication of the true material response. Additional limitations have been highlighted in another publication demonstrating the need for attention to experimental detail[26].

C. Acoustic Emission Measurements (AE)

The difference between chemical shrinkage and autogenous strain results in the formation of vapor-filled spaces in the system. The formation of vapor spaces (air-cavitation) can initiate only after a solid-structure develops in the system. It has been proposed that this cavitation can be detected as an acoustic event using acoustic sensors[20,27]. In this study, acoustic emission measurements were performed to detect acoustic cavitation in pastes with low *w/cm*, contained in a polyethylene mold[28]. A photograph of the sample holder is included in Figure 3. Although a standard for performing this test does not exist, it has been shown that acoustic emission is correlated to fundamental structure development in the material[28].

D. Electrical Conductivity of Cement Paste and Pore Solution

Electrical measurements have been used for 80 years to provide information about the hydration of cement-based materials[10,29,31]. Electrical conductivity measurements are a function of the pore solution chemistry (concentration), the pore solution volume, and the tortuosity of the pore system[30]. At early ages, the changes in pore solution volume and the pore solution conductivity are inversely related and their product is approximately constant[30], while the change in the connectivity of the water-filled pores is dramatic. This has been previously attributed to the formation of solid hydrates and cavitation of vapor spaces, which reduce moisture connectivity (conductivity) in the material[31]. The dramatic change in the rate of conductivity as the system hydrates can be used to interpret structure formation[31]. A standard does not currently exist for measuring the conductivity of cementitious materials in the field.

In this study, the electrical conductivity of cement pastes was measured using cylindrical paste specimens (Figure 4)[5,31,32]. The impedance response of each specimen was measured using an impedance gain phase analyzer. The bulk resistance (R_b) obtained from the impedance response was used to determine the material's conductivity after normalizing for the effects of specimen and electrode geometry[33]. In addition to measurements of paste conductivity, the conductivity of extracted pore solutions was also measured, using solutions extracted at early ages using nitrogen-filtration for young pastes or a high-pressure steel-die for mature pastes[34]. The conductivity of the extracted pore-solution was measured using a conductivity cell connected to the impedance analyzer[35,36]. Electrical conductivity measurements are sensitive to temperature and pore solution conductivity; consequently, it is important that the measurements be performed under nearly isothermal conditions[32].

E. Vicat Setting Tests (ASTM C191)

The Vicat setting test is the most commonly used test method to identify the initial and final setting times for hydrating cementitious mixtures. It measures the change in the penetration depth of a stylus under a constant applied load as increasing structure formation acts to reduce the extent of penetration into the specimen. The test identifies initial and final set at penetration depths of 25 mm and 0 mm, respectively, for pastes having a normal consistency (ASTM C191). In this study, initial and final setting times were assessed for cement pastes using this technique. A standard test method, ASTM C191, exists for penetration resistance testing of cement pastes. A specific concern of the Vicat test is that the time of initial and final set assessed using this technique is somewhat arbitrarily defined and may not correspond to a specific aspect of structure formation in the system.

F. Ultrasonic Pulse Conduction

The idea of using ultrasonic wave velocity measurements to determine setting times was initially described in the early 1980s[37]. Researchers have also described the use of shear waves[38] and longitudinal waves[39] to determine the setting times of concrete. Ultrasonic wave velocities depend on the density and connectivity of the material being tested. An increase in material density results in increased wave speed. This can be used to indicate the onset of structure formation and elastic property development (dynamic modulus) in cement systems[7,40]. At early ages, the compressional wave velocity is dominated by the fluid (interconnected) phase, however upon formation of a percolated-structure composed of solid hydrates; the compressional wave preferentially propagates through the interconnected solids[40]. The increase in compressive wave velocity measured at this time can be correlated to solid structure formation in the material[36].The compressional wave velocity at early ages is influenced by the presence of air in the system. A standard procedure, ASTM C597, exists for condition assessment of concrete elements using ultrasonics; however, this is not prescribed for early age material assessment.

In this study, the transmission method was used to perform ultrasonic measurements on cement pastes cast in a mold 25 mm thick, provided with piezoelectric transducers (Figure 5)[41]. Ultrasonic wave measurements were performed using a velocity meter connected to a digital oscilloscope. A personal computer was interfaced to the system to perform data acquisition by capturing the obtained waveform[42]. Ultrasonic wave measurements are susceptible to temperature effects due to the comparatively large sample size. In addition, it is important to minimize loss of contact with the transducers caused due to the sample's changing volume. The samples used in this study were neat, de-aired cement paste mixtures so as to negate the effects of entrapped air on the ultrasonic wave's transmission velocity.

G. Rheology Measurements

With increasing hydration and the formation of hydration products, the density and viscosity of a cementitious material increase leading to an increase in its flow resistance. The increase in flow resistance can be measured by assessing the changes in yield stress and plastic viscosity of the material. The rheological response of cementitious mixtures is also related to practical

considerations such as the ability to pump or finish the material[13,43,44,45,46]. A standard procedure does not currently exist to assess the rheological response of cementitious mixtures. However, ASTM Sub-Committee C01.22 is discussing the development of a standard for assessing the rheological properties of cementitious mixtures.

In this study, the rheological properties of cement pastes were assessed using a parallel-plate rheometer (Figure 6) using the stress-growth measurement technique[17,47]. The stress growth test is characterized by the material being sheared at the lowest shear rate possible (0.18 s^{-1} in this study)[13] and the resulting stress being measured from the time of casting. An illustration of the rheometer is provided in Figure 6. Rheological measurements are influenced by the configuration of the rheometer and by the consistency (fluidity, bleeding) of the cement paste.

H. Isothermal and Semi-Adiabatic Conduction Calorimetry

Cement hydration is an exothermic process. Monitoring the heat release signature of a hydrating mixture can be used to determine the rate and extent of hydration experienced by the sample. This information is useful in determining the progress of chemical reactions. Isothermal power curves, or hydration profiles, can provide information relative to the setting characteristics of a hydrating cementitious mixture. A draft procedure has been proposed (ASTM Subcommittee 01.26 Heat of Hydration) to standardize measurement of the heat release response of cementitious mixtures.

A TamAir* isothermal calorimeter was used to determine the heat that was dissipated during the hydration reaction under a constant temperature condition (23°C). The thermal power and cumulative energy measured were used to assess the kinetics and the extent of hydration experienced by the cementitious specimen. It should be noted that isothermal conduction calorimetry is extremely sensitive to the mixing action used in preparation of the mixtures, and is applicable only for the evaluation of cement pastes and mortars, due to sample size limitations.

An alternative to isothermal calorimetry is to utilize semi-adiabatic calorimetry to characterize the early-age performance of cement-based materials. Just beyond the induction period, the cement hydration reactions accelerate rapidly, causing a dramatic temperature rise in a specimen maintained under semi-adiabatic conditions. Thus, the occurrence of this temperature rise can be used as one indication of the end of the induction period and with proper calibration may be used to predict setting times[48,49,50,51]. This calibration is necessary for each mixture as it describes the extent of reaction that occurs before setting can occur and this varies depending on water-to-cement ratio and particle dispersion as described in Section 4 in the second paper in the series[57]. The experimental setup for semi-adiabatic calorimetry measurements can be quite simple, with acceptable results having been obtained using a coffee cup with a single thermocouple or thermometer imbedded in the cementitious sample.

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*Commercial equipment, instruments, and materials mentioned in this report are identified to foster understanding. Such identification does not imply recommendation or endorsement by Purdue University or The National Institute of Standards and Technology (NIST), nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

I. Restrained Ring Testing

If autogenous deformations are prevented due to external restraint, residual stresses develop in the material. The development of a residual stress implies the development of finite elastic properties and a solid-skeleton (backbone) that can support a stress in the system. ASTM C1581 describes a method to assess residual stress development when volume changes are restrained. However, some cementitious systems exhibit an early age expansion that cannot be characterized using the standard ASTM C1581 procedure. This early age expansion causes the annular (ring) specimen to lose contact with the restraining inner ring until it shrinks back to its original position. A dual Invar ring test apparatus, shown in Figure 7, has been developed that can determine the magnitude of this early expansion by measuring the strain developed in the external ring, which acts to restrain the early expansion[3,5,52,53]. The dimensions of the annuli used in the dual ring test are smaller than the standard ring dimensions, and include an inner and an outer ring to apply restraint on the specimen as it shrinks due to hydration. The dual ring test uses Invar steel rings to minimize effects of temperature change, which are known to influence the results of the standard test. The dual ring testing apparatus[3,5,52,53] used in this investigation is capable of identifying the initiation and magnitude of residual stresses developed in the material from a few minutes after casting.

4. Hydration Modeling using CEMHYD3D

Computer models have been developed that simulate cement hydration and microstructure development. These simulations predict a wide range of properties that can be compared to experimental measurements, such as isothermal heat signature and chemical shrinkage. A three-dimensional (3-D) digital image model (CEMHYD3D, version 3.0) was used in this study to simulate microstructure development of cement pastes[54]. In CEMHYD3D, each volume element in a 3-D digital image of the microstructure represents a single cementitious phase, and thus each individual cement particle may be composed of multiple phases in agreement with the characteristics of real cement particles. The clinker phases are first distributed amongst the cement particles to match the phase volume fractions, phase surface fractions, and phase correlation functions of the cement of interest, as measured on phase-segmented images obtained by scanning electron microscopy (SEM) and x-ray element mapping (EDS)[55]. Hydration is then simulated by applying a cellular automata set of rules in a cyclic fashion to mimic the physical processes of dissolution, diffusion, nucleation, and surface precipitation. After each reaction cycle, phases are tabulated and a variety of physical quantities such as heat release and chemical shrinkage are computed.

For the present study, the measured particle size distribution and phase composition of the cement were utilized to create a starting paste microstructure, with flocculated particles (not containing a water-reducer), which was subsequently ‘hydrated’ in a virtual environment using the computer model. During hydration, the following outputs were monitored: chemical shrinkage, degree of hydration, phase volume fractions, and percolation of the total solids (to assess setting). Because the initial cement particles are flocculated (touching), a special percolation algorithm (burning algorithm) was used to examine setting behavior, by determining which particles have been bridged (connected) by hydration products. The chemical shrinkage results were compared to experimental values in order to calibrate the model’s kinetic factor that

converts between the model's cycles of hydration and real time (h)[54]. Previously, the model has provided favorable comparisons to experiments for a variety of early-age and later age properties of pastes and mortars[56]. Figure 8 provides examples of two-dimensional cross section images from the three-dimensional model microstructures.

5. Summary and Conclusions

This paper has described techniques capable of fundamentally assessing solidification and the extent of structure development in cement-based materials. A detailed summary of these techniques is provided in Table 1. Each technique probes a different physical aspect of the system, but from a fundamental viewpoint it should be possible to correlate the material response as measured by each technique to identify the fluid-solid transition in cement systems. The experimental and numerical techniques to identify the time of solidification were performed on a single material and the results will be compared in the second paper in the series[57].

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Table 1: Summary of Experimental and Modeling Techniques

Technique	Stimulus/Curing Conditions	Measured Material Response	Destructive (Yes/No)	Performance (Lab/ Site)	Interpretation of Solidification	Interpretation of Hydration	Technique Variability	ASTM Standard (Conceptual)
Chemical Shrinkage	Passive Saturated	Volume of imbibed water	No	Lab	Divergence between chemical and autogenous deformation curves	Ratio of instantaneous to ultimate internal volume change	±5 %, based on three tests between 1 h and 24 h	ASTM C1608
Autogenous Strain	Passive Sealed	Change in external volume	No	Lab	Divergence between chemical and autogenous deformation curves	N/A	±5 %, based on three tests between 1 h and 24 h	Under Development
Cement Paste Conductivity	Application of a low voltage AC stimulus Sealed	Rate of change in conductivity	No	Lab	Maximum change in rate on the conductivity curve	N/A	±5 % for different samples of a given mixture	N/A
Acoustic Emission	Passive Sealed	Cavitation of Air Voids	No	Lab/Site	Dramatic increase in acoustic events	N/A	N/A	N/A
Vicat Needle	Penetration by a weighted needle Sealed	Penetration Resistance	Yes	Lab/Site	Penetration depth of 25 mm (Initial Set)	N/A	12 % for a single operator (ASTM C191)	ASTM C191
Ultrasonic Pulse Conduction	Transmission of an Ultrasonic Pulse Sealed	Increase in wave velocity	No	Lab/Site	Dramatic increase in pulse conduction velocity	N/A	±5% for different samples of the same mixture	ASTM C597
Cement Paste Rheology	Application of a shear stress at a specific shear rate on the specimen Sealed	Increase in measured yield stress	Yes	Lab	Dramatic increase in yield stress	N/A	±10 % for tests on same mixture	Under Development
Isothermal Calorimetry	Passive Sealed	Heat evolution signature	No	Lab	N/A	Ratio of instantaneous to ultimate heat release	±2 % for tests on same mixture	Under Development
Semi-adiabatic Calorimetry	Passive Sealed	Temperature Evolution Profile	No	Lab/Site	Dramatic increase in sample temperature	Energy Balance	Depends on heat loss of experimental setup	N/A
Restrained Shrinkage Testing	Passive Sealed	Change in Strain	Yes	Lab	Development of restrained shrinkage strain	N/A	±10 % for tests on same mixture	ASTM C1581
Numerical Modeling (CEMHYD3D)	Generation of initial state of microstructure Sealed/Saturated	Increasing microstructure development (percolation)	Virtual Testing	Lab	Percolation of solids	Mass fraction of cement clinker reacted	±2 % for DOH, ±30 min for set, subject to initial calibration	N/A

Figures

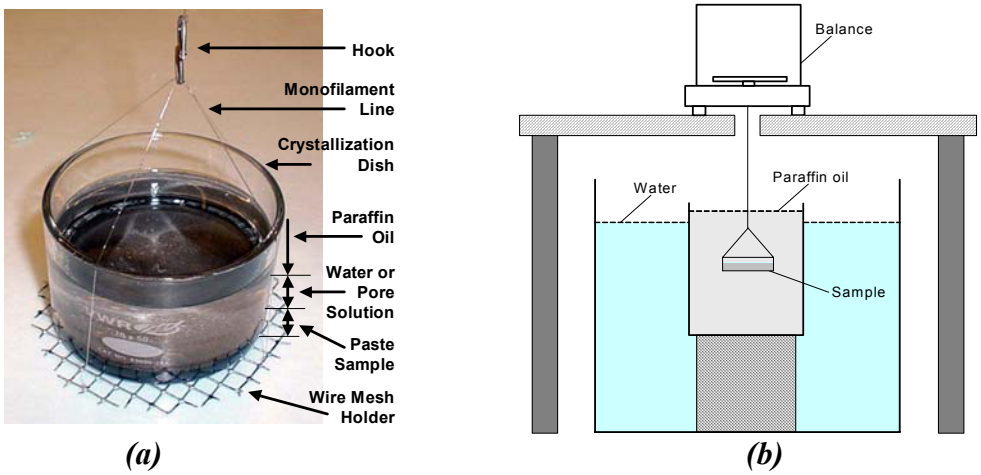


Figure 1: An illustration of procedures to measure chemical shrinkage (a) a photo of the chemical shrinkage test specimen (b) an illustration of the buoyancy method for measuring chemical shrinkage.

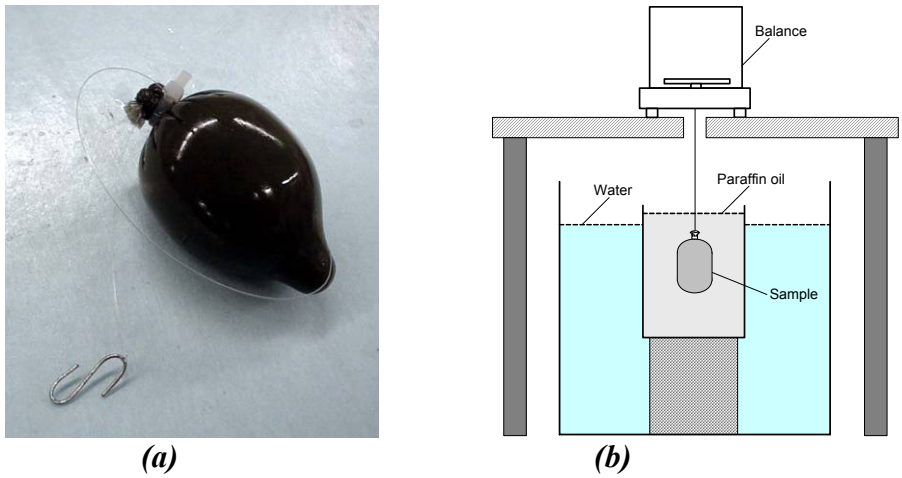
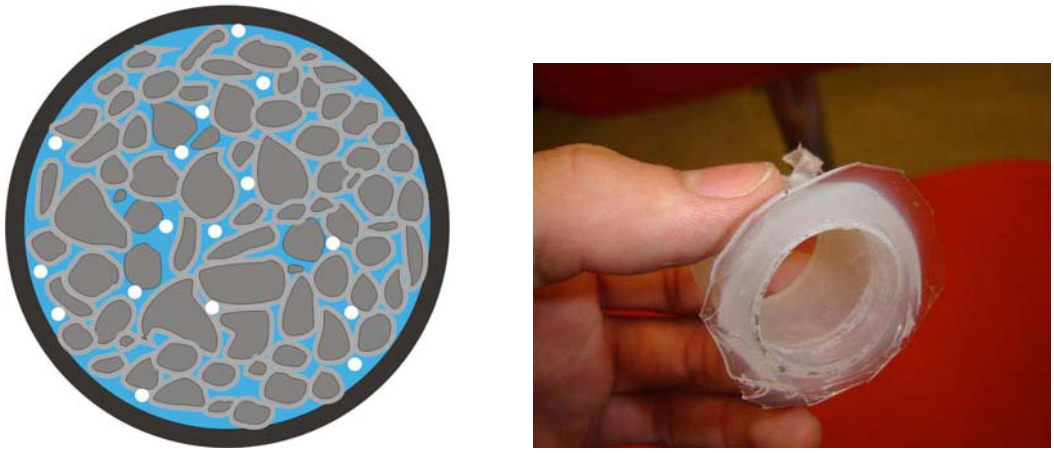
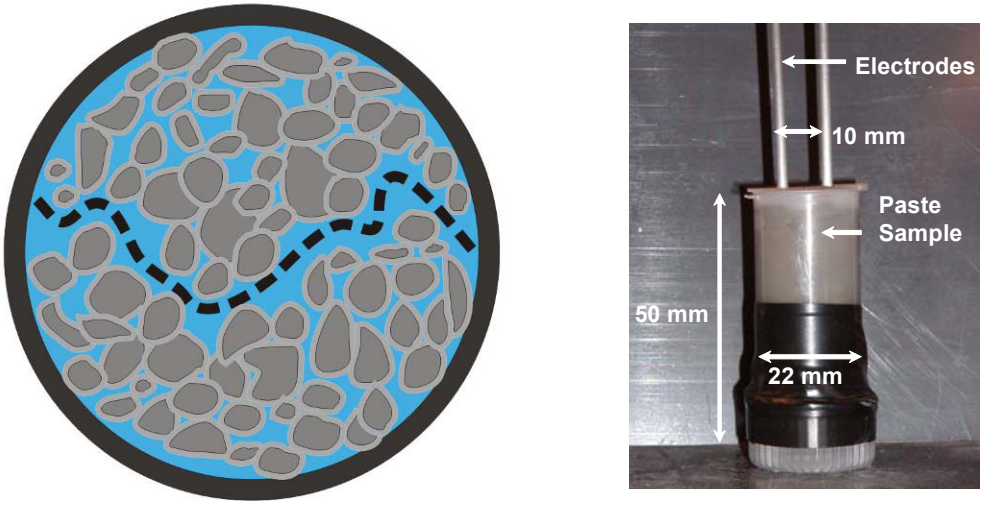


Figure 2: An illustration of procedures to measure autogenous shrinkage (a) a photo of the autogenous shrinkage test specimen (b) an illustration of the buoyancy method for measuring autogenous shrinkage.



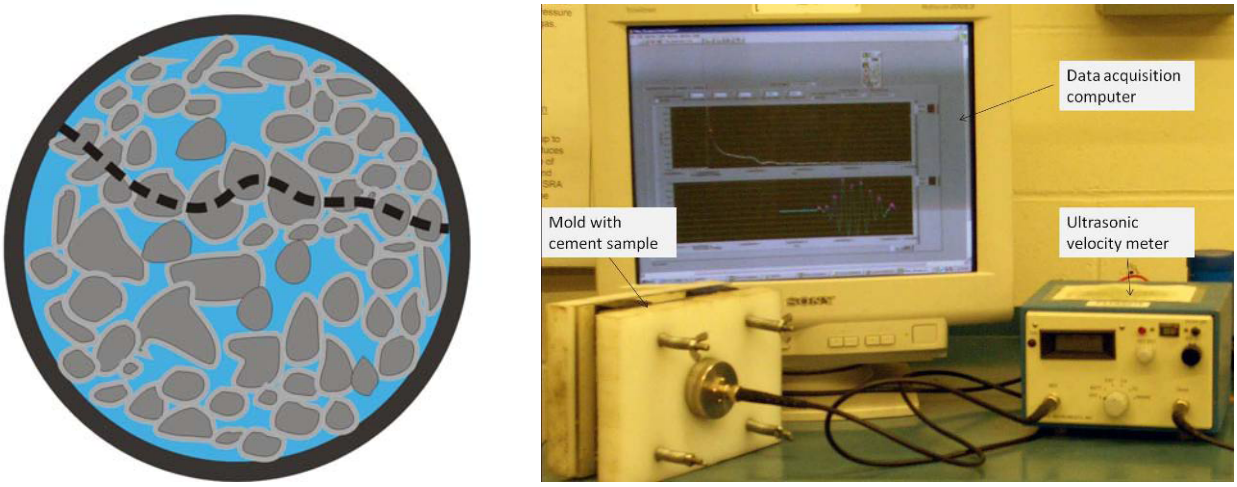
(a) ***(b)***

Figure 3: (a) An illustration of a hydrating sample with cement particles (grey) and vapor spaces (white) in the pore solution (blue) and (b) The sample holder used to contain the cement paste for acoustic emission measurements.



(a) ***(b)***

Figure 4: (a) An illustration of the tortuous electrical conduction path in a hydrating sample (b) The plastic vial containing cement paste provided with embedded electrodes for the measurement of electrical conductivity.



(a) ***(b)***

Figure 5: (a) A conceptual illustration of the ultrasonic wave conduction path through a hydrating cement paste sample (b) The testing apparatus used to measure ultrasonic wave velocity.

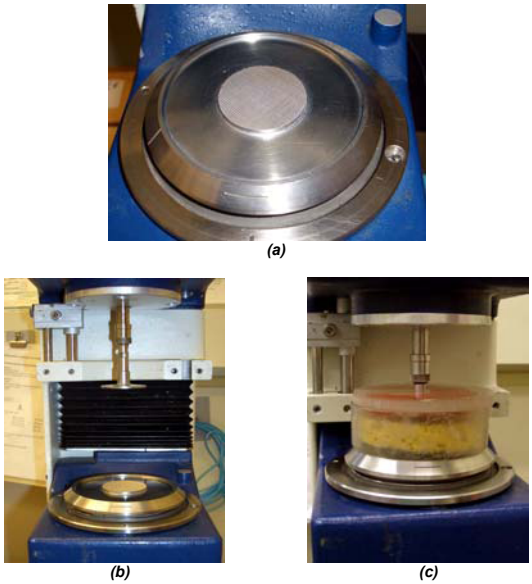


Figure 6: (a) The serrated lower plate of the rheometer (b) The parallel plate rheometer used in the stress growth test, (c) The environmental control chamber used to contain the sample for the duration of the test.

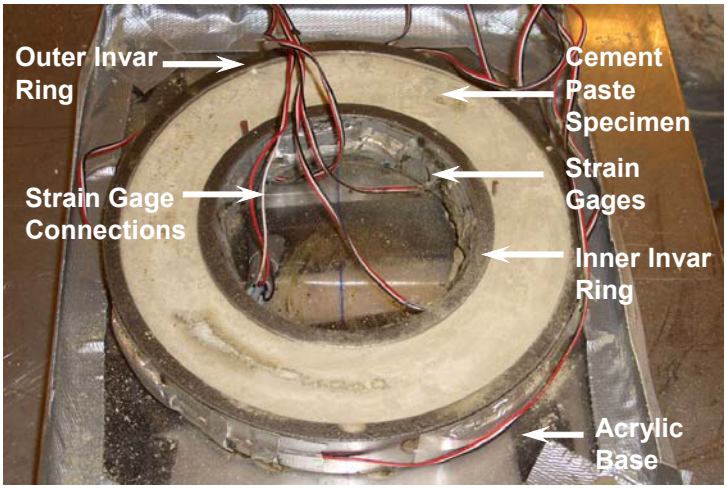
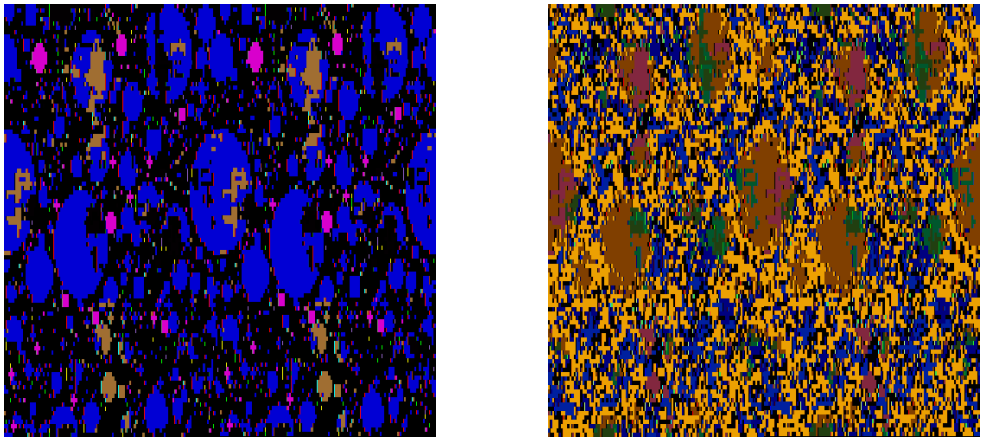


Figure 7: An illustration of the dual ring setup used to measure restrained shrinkage.



(a) ***(b)***

Figure 8: Two-dimensional cross-section images from the three-dimensional microstructures generated by CEMHYD3D (a) initial microstructure (b) microstructure at 50 % hydration (Color Code for Images: Red – C_3S, Aqua – C_2S, Green – C_3A, Yellow – C_4AF, Gray – Gypsum, Orange – CSH, Blue – $Ca(OH)_2$, Black – Water-filled Porosity and White – Empty Porosity)

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