ASCE Journal of Materials in Civil Engineering, 21 (9), 512-517, 2009. Early-Age Properties of Cement-Based Materials: II. Influence of Water-to-Cement Ratio

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Abstract

The influence of water-to-cement mass ratio (w/c) on early-age properties of cementbased materials is investigated using a variety of experimental techniques. Properties that are critical to the early-age performance of these materials are tested, including heat release, semiadiabatic temperature, setting time, autogenous deformation, and strength development. Measurements of these properties using a single cement are presented for four different w/c, ranging from 0.325 to 0.425. Some of the measured properties are observed to vary widely within this range of w/c ratios. The heat release and setting time behaviors of cement pastes are contrasted. While early-age heat release is relatively independent of w/c, the measured setting times vary by several hours between the four w/c investigated in this study, indicating the fundamental differences between a physical process such as setting and heat release which is purely a quantification of chemical reaction. While decreasing w/c certainly increases compressive strength at equivalent ages, it also significantly increases autogenous shrinkage and may increase semi-adiabatic temperature rise, both of which can increase the propensity for early-age cracking in cement-based materials.

Introduction

One of the major variables influencing the performance of a concrete mixture is its waterto-cement mass ratio (w/c). From the earliest days of concrete, the major influence of w/c on compressive strength has been recognized (Feret 1897, Abrams 1918). Because the w/c directly controls the volume of water available for hydration per unit volume of cement and also establishes the initial interparticle spacing between cement particles, it will influence a wide variety of early-age properties such as setting time, semi-adiabatic temperature rise, and autogenous shrinkage. The latter two variables can potentially be major contributors to early-age cracking of cement-based materials (ACI 2008). This paper contrasts these performance properties for four different w/c cement pastes and mortars prepared from a single cement. In part I of this series, a similar study was conducted with cement fineness as the independent variable (Bentz et al. 2008).

Experimental

For this study, a single Type I/II portland cement was used, while the w/c of the cement pastes and mortars was set at values of 0.325, 0.350, 0.400, and 0.425. This range of w/c was

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selected based on having mixtures that did not exhibit excessive bleeding while still providing adequate workability without the addition of any chemical admixtures. The measured oxide composition and Bogue potential phase composition, as provided by the manufacturer, are listed in Table I. A Blaine fineness of 380 m²/kg was reported by the manufacturer. The cement specific gravity was measured at the National Institute of Standards and Technology (NIST) using ASTM C188 (ASTM International 2003); two replicates each gave a value of 3220 kg/m³. The measured particle size distribution (via laser diffraction) of the selected cement is given in Figure 1.

Oxide or Property	Mass fraction
CaO	0.6301
SiO_2	0.2027
Al ₂ O ₃	0.0473
Fe ₂ O ₃	0.0351
SO_3	0.0286
MgO	0.0315
Na equivalent	0.54
Bogue - C ₄ AF	0.107
Bogue - C ₃ A	0.066
Bogue - C ₃ S	0.575
Bogue - C_2S	0.148

Table I. Cement oxide composition and Bogue potential phase mass fractions as provided by the cement manufacturer

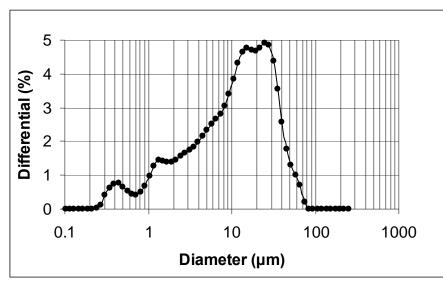


Figure 1. Measured differential particle size distribution for the cement. The x-axis indicates an equivalent spherical particle diameter and the y-axis the mass % at each given diameter. The shown results are the average of six individual measurements and the error bars (one standard deviation) would fall within the size of the shown symbols.

For measurements of calorimetry and setting time, cement pastes were prepared using a high shear blender. Mortars were prepared according to the ASTM C 305-06 procedures (ASTM

International 2006a) using a blend of four sands, each with a specific gravity of 2610 kg/m³. The mortar mixture proportions for the four different w/c mixtures are provided in Table II. In each mortar mixture, the same volume fraction of sand (about 54.8 %) was maintained; the water absorptions of the silica sands were assumed to be negligible. The w/c = 0.325 mortar mixture exhibited a very low workability that made it somewhat difficult to prepare the mortar cubes and corrugated tubes for strength and autogenous deformation evaluations, respectively. The average measured air contents of the fresh mortars was 3.1 %, with a range of 2.7 % to 3.4 % observed for the four different w/c mixtures.

Material	w/c = 0.325	w/c = 0.350	w/c = 0.400	w/c = 0.425
Type I/II cement	1800.0 g	1800.0 g	1800.0 g	1800.0 g
Water	585.0 g	630.0 g	720.0 g	765.0 g
F95 fine sand ^A	903.7 g	940.5 g	1008.9 g	1047.4 g
Graded sand (ASTM C 778 ^B)	686.8 g	714.8 g	766.8 g	796.0 g
20-30 sand (ASTM C 778 ^B)	686.8 g	714.8 g	766.8 g	796.0 g
GS16 coarse sand ^A	1337.5 g	1391.9 g	1493.2 g	1550.1 g

Table II. Mortar mixture proportions used in the study

^AF95 and GS16 correspond to sand supplier designations.

^B(ASTM International 2006b).

The following measurements were conducted on the cement paste and mortar specimens: 1) Isothermal calorimetry – the heat of hydration was measured during the course of 7 d on premixed (as opposed to being mixed in situ in the calorimeter cells) sealed cement paste samples with a mass between 4.9 g and 5.4 g or about 8 g of pre-mixed sealed mortars using a TAM Air Calorimeter (Certain commercial products are identified in this paper to specify the materials used and procedures employed. In no case does such identification imply endorsement by the National Institute of Standards and Technology, nor does it indicate that the products are necessarily the best available for the purpose.); to provide an indication of variability, two specimens from the same batch were evaluated in neighboring calorimeter cells for each experiment; in the results to follow, results are normalized per unit mass of cement in the sample, 2) Semi-adiabatic calorimetry – the semi-adiabatic temperature was measured during the course of 3 d on single sealed cement paste specimens with a mass of approximately 330 g using a custom-built semi-adiabatic calorimeter unit (Bentz and Turpin 2007); replicate specimens from separate batches have indicated a standard deviation of 1.4 °C in the maximum specimen temperature achieved during a 3 d test,

3) Time of setting – measured on single sealed cement paste specimens based on penetration of the Vicat needle according to ASTM C 191 (ASTM International 2007a); in the ASTM C 191 standard, the single laboratory precisions are listed as 12 min and 20 min for initial and final time of setting, respectively,

4) Compressive strength – measured at 1 d, 3 d, 7 d, and 28 d on mortar cube specimens cured in a saturated calcium hydroxide solution, according to the procedures in ASTM C 109 (ASTM International 2007b), but with a loading rate of 20.7 MPa/min, switching to deformation control (at the instantaneous deformation rate) once a stress of 13.8 MPa was reached; three specimens

prepared from a single batch were evaluated at each time, with the averages and standard deviations provided in the results to follow, and

5) Autogenous deformation – measured on triplicate or duplicate sealed mortar specimens prepared from a single batch, sealed in corrugated tubes (Jensen and Hansen 1995) (procedure is currently being standardized in ASTM subcommittee C09.68); in the draft standard, the single laboratory precision is listed as 30 microstrains for mortar specimens.

The initial three-dimensional microstructures based on these four different w/c will be significantly different. To illustrate this point, Figure 2 shows two-dimensional cross-section images from simulated three-dimensional starting microstructures (Bentz 1997) where the assumed spherical cement particle diameters follow the size distribution provided in Figure 1 and the particles have been flocculated in three-dimensional space (since no chemical admixtures were utilized in the current study). Each two-dimensional image is 100 µm by 100 µm. Qualitatively, the interparticle spacing (initial pore size) looks to be greater in the higher w/cmicrostructures. Using software available at http://ciks.cbt.nist.gov/cementspacing.html, the water-to-cement distance function (Bentz and Aitcin 2008) was simulated for each of these mixtures, with particle placement at totally random locations beginning with the largest particles. The water-to-cement distance function measures the volume fraction of the total water that is within a given distance of a cement particle surface. The results for this fractional volume of water are provided in Figure 3. The distance values for volume fractions of water of 0.9 and greater provide an indication of the sizes of the initial pores that will be emptied during selfdesiccation, for instance (Bentz and Aitcin 2008). Thus, this interparticle spacing (pore size) will have a large influence on the development of autogenous stresses and strains within the hydrating cement paste and mortar specimens (Bentz et al. 2001, Baroghel-Bouny et al. 2006).

Results and Discussion

Compressive Strength

The compressive strength results are considered to provide a frame of reference in which to consider the other early-age property measurements. As shown in Table III, the two lowest w/c consistently produce higher compressive strengths at all four testing ages. At the ages of 1 d and 7 d, the strengths of the w/c = 0.325 mortar cubes are slightly lower than those of the w/c = 0.350 cubes. This may be due to the low workability of the w/c = 0.325 mortar and difficulty in properly compacting the fresh mortar mixture into the cube molds, or to a reduction in the achievable degree of hydration due to space limitations as w/c decreases below about 0.38 in a saturated system (Taylor 1997).

Age	w/c = 0.325(MPa)	w/c = 0.350 (MPa)	w/c = 0.400 (MPa)	w/c = 0.425 (MPa)
1 d	$33.8(1.0)^{A}$	36.2 (1.4)	25.2 (0.4)	20.9 (0.1)
3 d	56.1 (1.8)	55.6 (2.4)	47.6 (1.5)	41.0 (0.4)
7 d	64.0 (4.4)	64.8 (1.0)	55.1 (1.6)	50.8 (1.0)
28 d	81.8 (4.4)	78.5 (2.2)	72.8 (1.4)	68.7 (3.4)

Table III. Compressive strength results for mortar cubes

^ANumbers in parentheses indicate one standard deviation as determined for the three replicate specimens tested at each age.

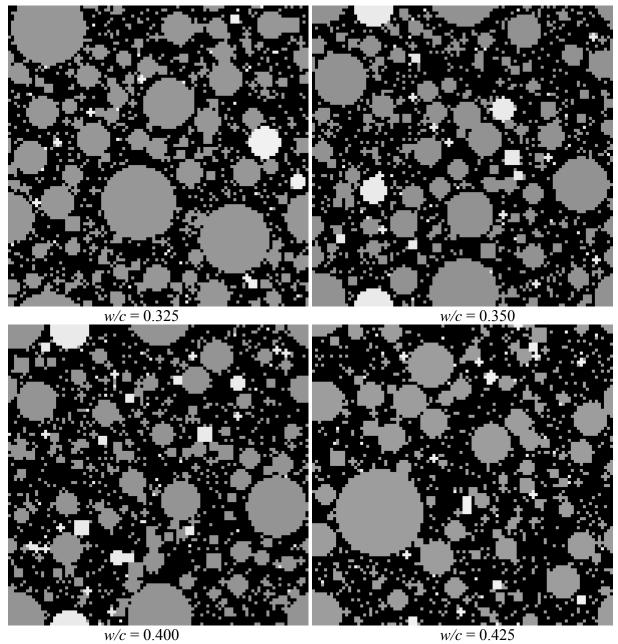


Figure 2. Single two-dimensional cross-sectional images (100 μ m by 100 μ m) from threedimensional simulated starting microstructures for cement pastes for the four different *w/c* investigated in this study (cement particles are grey and gypsum particles are white)

Isothermal Calorimetry and Setting Characteristics

Next, the heat release properties of the various mixtures are considered. The isothermal calorimetry results for the four different w/c pastes are provided in Figures 4 and 5, in terms of the cumulative heat release and the heat release rate at early ages respectively. For the cumulative heat release results, when normalized by the mass of cement in each sample to relate heat release to degree of cement hydration, the four curves overlap one another for the initial 12 h before approaching different values at later ages. It is well known that for w/c below about 0.44, there is insufficient water to provide complete hydration of the anhydrous cement under

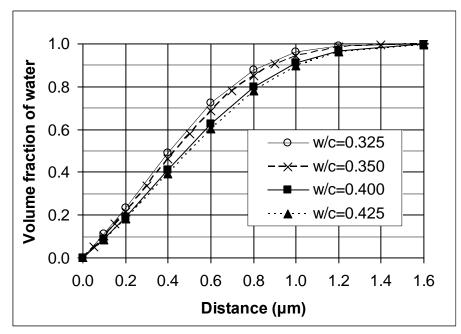


Figure 3. Water-to-cement distance functions (Bentz and Aitcin 2008) computed for threedimensional starting microstructures (200 μ m by 200 μ m by 200 μ m) for the four different *w/c* cement pastes investigated in this study

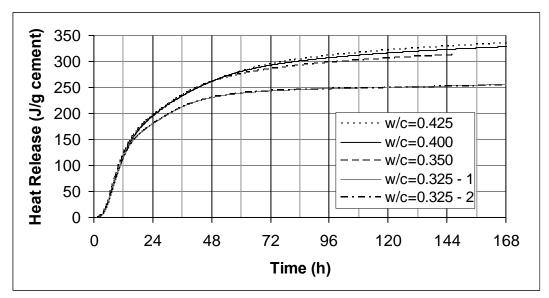


Figure 4. Cumulative heat release for 7 d from isothermal calorimetry for the cement pastes with four different w/c. Two curves that basically overlap one another are shown for the w/c=0.325 paste to provide an indication of variability between duplicate specimens.

sealed curing conditions (Taylor 1997). Because the isothermal calorimetry specimens are sealed with no external curing water supplied, they will self-desiccate due to the chemical shrinkage that accompanies the cement hydration reactions (Bentz 1997). This will decrease the ongoing hydration rates, an effect that will be more pronounced in lower w/c pastes. Thus, in Figure 4, the heat release curves for w/c = 0.400 and w/c = 0.425 basically overlap one another

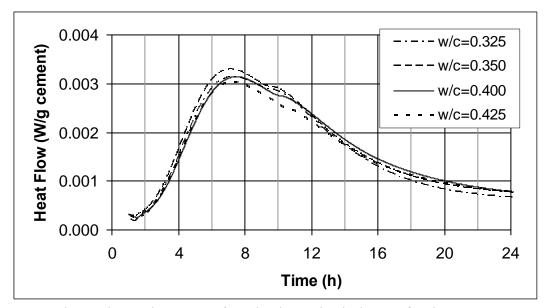


Figure 5. Early-age heat release rates from isothermal calorimetry for the cement pastes with four different w/c

for the entire 7 d of hydration examined in this study, as during these first 7 d of hydration, neither paste becomes water limited. The w/c = 0.350 paste breaks away from these two curves after about 2 d of hydration, while the w/c = 0.325 curve diverges from the others much earlier, after only about 12 h of hydration, due to an inadequate supply of water to maintain hydration.

The heat release rate curves for the first 24 h of hydration shown in Figure 5 are quite similar for the four different w/c pastes examined in this study. Previously, Sandberg and Roberts (2005) have also observed quite similar heat release rate curves for pastes prepared with a single cement with w/c of 0.35, 0.40, and 0.45. While the heat release results are nearly independent of w/c for the pastes prepared in this study, the setting times of the pastes as assessed using Vicat needle penetration are strongly influenced by w/c, as shown in Figure 6. The initial setting times (heavy dashed line in Figure 6 indicating a penetration of 25 mm) are seen to vary by over 1.5 h for the range of w/c investigated in this study, while the final setting times (no penetration) vary by about 2 h. Clearly, the degree of hydration necessary to produce setting (a physical process) is a function of w/c, with higher w/c requiring more hydration, likely due to their increased interparticle spacing (Figures 2 and 3).

While it appears clear from the results in Figures 5 that isothermal calorimetry (a measure of chemical reaction) cannot provide a reliable indication of setting (a physical process), as shown in Figure 6, for cement **pastes** of different w/c, some other research groups are currently using it as a technique to predict the setting times of mortars and concretes as measured using ASTM C403 (ASTM International 2006c). To investigate this apparent contradiction further, the measurements were repeated for mortar mixtures (as provided in Table II) for the same values of w/c, using the ASTM C807 Standard Test Method for Time of Setting of Hydraulic Cement Mortar by Modified Vicat Needle (ASTM International 2005). The heat release rate results for these four mortars are provided in Figure 7. For the mortars, as compared to the pastes in Figure 5, a greater dispersion between the four curves is observed. Taking the first maximum in

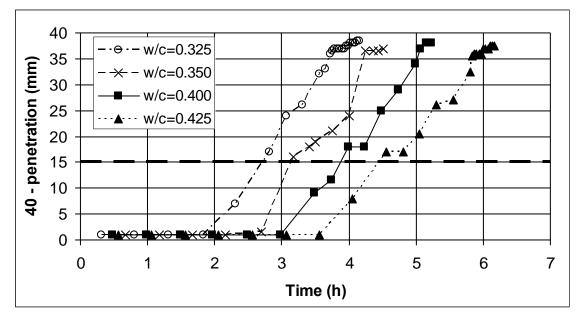


Figure 6. Vicat setting (plotted as 40 - needle penetration) results for the cement pastes with four different w/c; dashed horizontal line indicates initial set per the ASTM test method

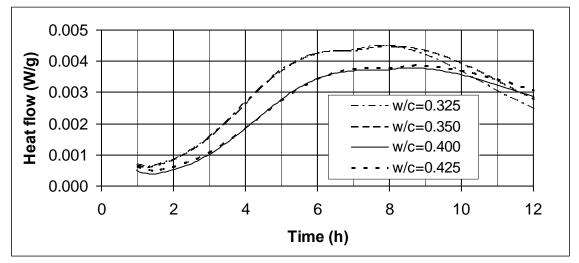


Figure 7. Early-age heat release rates from isothermal calorimetry for the mortars with four different w/c

the derivative of the heat release rate curve as an indication of set, Figure 8 provides a plot of these "thermal times" vs. the times of set measured using the modified needle. The results are certainly more promising than in the case of cement pastes, but do not fall on a 45 degree line, indicating that while correlation exists between the two times, they are not identical and cannot simply be used interchangeably. Results from other groups have indicated a similar correlation between ASTM C403 setting times and these thermal indicators of setting, but with relationships that differ significantly from one cement to another, further supporting the observation that the relationship between setting and thermal indications of hydration is not a simple identity function. In summary, based on the results presented in this study, for cement **pastes** prepared in the laboratory, isothermal calorimetry is not a reliable indication of setting time for w/c in the range

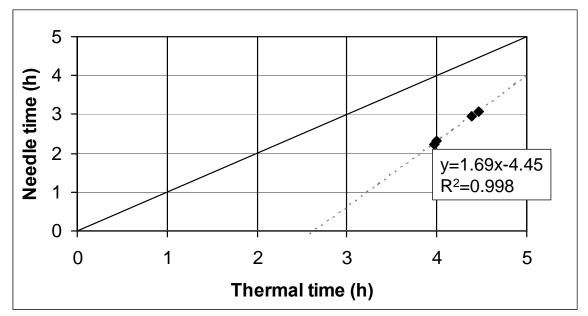


Figure 8. ASTM C 807 time of set vs. time of maximum in derivative of heat release rate for the four cement mortars with different w/c. Dark line indicates an identity relationship and dashed line indicates best linear fit.

of 0.325 to 0.425, as only minimal variation between the isothermal calorimetry curves is observed for w/c in this range. Conversely, for **mortars**, an adequate correlation is observed between setting time and the time of the first maximum in the derivative of the heat release rate, but it is likely that calibration would be required to determine the specific correct relationship for each individual cement, and possibly also for each cement-admixture combination. Recently, similar conclusions have been reached for cement pastes regarding chemical shrinkage measurements (another measure of chemical reaction) and setting time (Sant et al. 2008).

Semi-Adiabatic Temperature

The influences of w/c on thermal properties at early ages were further investigated using semi-adiabatic calorimetry measurements on cement pastes. Semi-adiabatic calorimetry may provide an indication of the susceptibility of a mixture to early-age thermal cracking (Bentz et al. 2008, ACI 2008, Bentz and Peltz 2008). The plots of temperature vs. time for the four cement pastes are provided in Figure 9. A change in w/c has several distinct influences on the semiadiabatic temperature curves. First, because water has a much larger heat capacity than anhydrous cement, 4.18 J/(g·K) vs. 0.75 J/(g·K) (Bentz 2007), a smaller temperature rise would be expected when w/c is increased (Bentz and Peltz 2008). Second, less cement per unit volume also means less heat generation within the fixed volume semi-adiabatic calorimeter specimen holder when w/c is increased. Conversely, the influences of w/c on the achievable long term degree of hydration as discussed above may result in less heat being produced once w/c falls below about 0.36. These effects are well illustrated by the results in Figure 9 where peak temperature first increases as the w/c is lowered from 0.425 to 0.400 to 0.350, but then exhibits no further increase as w/c is further lowered to 0.325, as the lower heat capacity and higher cement content of the paste are finally offset by the decreased (achievable) hydration at the lowest w/c examined in this study.

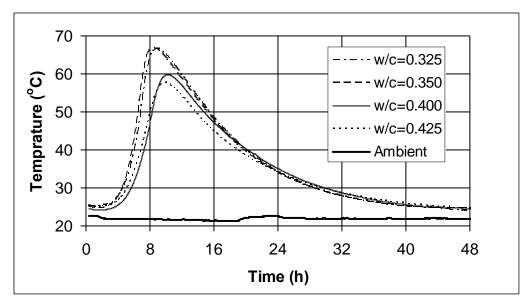


Figure 9. Semi-adiabatic temperature during the first 48 h of hydration for the cement pastes with four different w/c

Autogenous Deformation

Finally, the autogenous deformations of the four mortar mixtures are considered. Once again, as shown in Figure 10, w/c has a large influence on this early-age property of cementbased materials. The autogenous deformation measured for each mortar mixture is a competition between an autogenous shrinkage due to self-desiccation in these sealed corrugated tube specimens and an expansive process that is not well understood, but is conjectured to be due to ettringite and/or calcium hydroxide crystal formation and growth or perhaps imbibition of water by the cement hydration (gel) products (Bentz et al. 2001, Baroghel-Bouny et al. 2006). Expansion at early ages could also be due to thermal expansion as energy is released by the cement hydration reactions, but for the 25 mm diameter corrugated tubes employed in this study, temperature changes at early ages should be less than 2 °C according to the draft ASTM standard. In actuality, by inserting a single thermocouple into the center of the corrugated molds, the following temperature changes were measured between the time of set and 24 h for the w/c=0.325, 0.35, 0.4, and 0.425 mortars: 0.9 °C, 1.0 °C, 0.9 °C, and 1.0 °C. A 1 °C temperature change should result in an expansion/contraction of about 10 to 20 microstrains, much less than the expansions indicated in Figure 10.

It is clear that as w/c decreases, the initial interparticle spacing decreases (Figures 2 and 3), which will increase the magnitude of the autogenous stresses induced by the menisci in the partially water-filled capillary pores. It is less clear if the expansive processes are influenced by w/c, but the results in Figure 10 do clearly indicate that any change in early-age expansion with w/c is far overwhelmed by the increase in autogenous shrinkage as w/c is decreased. For each cement (having a given degree of fineness), there will be a critical w/c below which the measured long term (28 d) autogenous deformation will exhibit a shrinkage and above which an expansion will be measured (Baroghel-Bouny et al. 2006, Bentz et al. 2008). For the cement employed in this study, this "threshold" w/c (Baroghel-Bouny et al. 2006) would be slightly above 0.425, as the w/c = 0.425 mortar exhibited only a small autogenous shrinkage of about -30 microstrains after 28 d hydration.

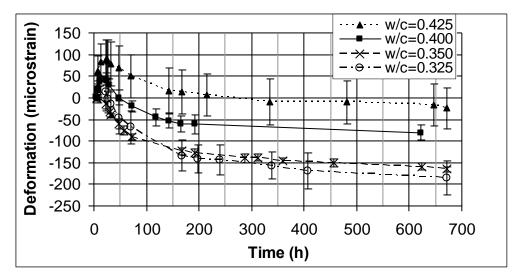


Figure 10. Autogenous deformation results for the four mortar mixtures. Error bars indicate one standard deviation as determined for the triplicate specimens of each mixture

Recently, Cusson has advocated the utilization of the (net) difference between the maximum (peak) and minimum (achieved post peak) deformations achieved during the first 7 d of curing as an effective measure of the risk of cracking in a concrete structure, as a concrete typically reaches a zero-stress state sometime after the peak (expansion) is achieved, but prior to the autogenous deformation returning to zero (or achieving its minimum value) (Cusson 2008). Beyond this zero-stress time, tensile stresses develop and build under restrained conditions and may ultimately lead to early-age cracking if the tensile strength of the concrete is exceeded at any time (ACI 2008, Cusson 2008). For the four mixtures examined in this study, these values of net autogenous shrinkage, ($\varepsilon_{min}-\varepsilon_{max}$), are provided in Table IV. The magnitudes of these net autogenous shrinkage values monotonically decrease with increasing *w/c*, supporting the generally accepted hypothesis that lower *w/c* mixtures will have an increased autogenous shrinkage and likely be more susceptible to the early-age cracking that such shrinkage may induce if movement is restrained.

Mortar mixture	$(\varepsilon_{\min} - \varepsilon_{\max})$ (Microstrains)
w/c = 0.325	-151
w/c = 0.350	-127
w/c = 0.400	-100
w/c = 0.425	-75

Table IV. Net autogenous shrinkage strains at 7 d for the four mortar mixtures

Conclusions

A comprehensive study of a variety of early-age properties of cement pastes and mortars with w/c ranging from 0.325 to 0.425 have been conducted including compressive strength, isothermal calorimetry, semi-adiabatic temperature, setting time, and autogenous deformation. These studies have indicated that:

- For cement pastes prepared in the laboratory, isothermal calorimetry may not be a reliable indication of setting time for w/c in the range of 0.325 to 0.425, as only minimal variation between the isothermal calorimetry heat flow curves is observed for w/c in this range.
- For mortars prepared in the laboratory, correlation can be established between isothermal calorimetry and setting time measurements for w/c in the range of 0.325 to 0.425, but the best fit relationship is not a simple identity function (e.g., slope greater than 1 and non-zero intercept).
- Decreasing w/c will increase the peak temperature achieved during semi-adiabatic hydration except for w/c less than about 0.38, where the reduced degree of achievable hydration will limit the heat release and consequent temperature rise.
- Decreasing w/c increases the autogenous shrinkage of mortars cured under sealed conditions, both in terms of the absolute deformation achieved after 28 d and the net shrinkage experienced during the first 7 d of hydration.

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