

Early-Age Properties of Cement-Based Materials: I. Influence of Cement Fineness

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Abstract

The influence of cement fineness on early-age properties of cement-based 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, temperature rise, chemical shrinkage and autogenous deformation. Measurements of these properties for two cements of widely different fineness are supplemented with other performance measures, specifically acoustic emission measurements to listen for microcracking occurring in high performance $w/c = 0.35$ mortars and dual-ring paste shrinkage measurements conducted under sealed conditions to assess residual stress development. The measured properties are observed to be quite different for the coarse and the fine cement. The current emphasis on high early-age strength within the construction industry may result in the specification of cements that are more prone to early-age cracking.

Introduction

It is an incontrovertible fact that the fineness of Portland cements have increased during the past 50 years and are continuing to increase [1,2]. Figure 1 summarizes the mean values from three surveys as presented by the Portland Cement Association [2] and also includes individual results from the Cement and Concrete Reference Laboratory (CCRL) proficiency sample program [1] compiled during the past 40 years. While it can be argued that there is no guarantee that the cements selected by CCRL are representative of the cements available from the industry as a whole, taken together, all of the results in Figure 1 clearly indicate the trend of increasing cement fineness. Both regression lines in Figure 1 extrapolate to a typical Blaine fineness for a Type I/II cement being nearly $400 \text{ m}^2/\text{kg}$ by the year 2010. Many cements with a fineness of $400 \text{ m}^2/\text{kg}$ to $420 \text{ m}^2/\text{kg}$ are currently available. One of the main reasons for the move towards finer cements has been the ever increasing emphasis on high early-age strengths and fast track construction by much of the industry. Finer cements, with their higher surface area, are more reactive at early ages, producing the desired higher early-age strengths. Since most cement producers are hesitant to produce a wide range of products, the same Type I/II cements that are manufactured for high early-age strength applications (high rise construction, etc.) are also employed in pavements and bridge decks, where long term durability may be much more critical than early-age strength.

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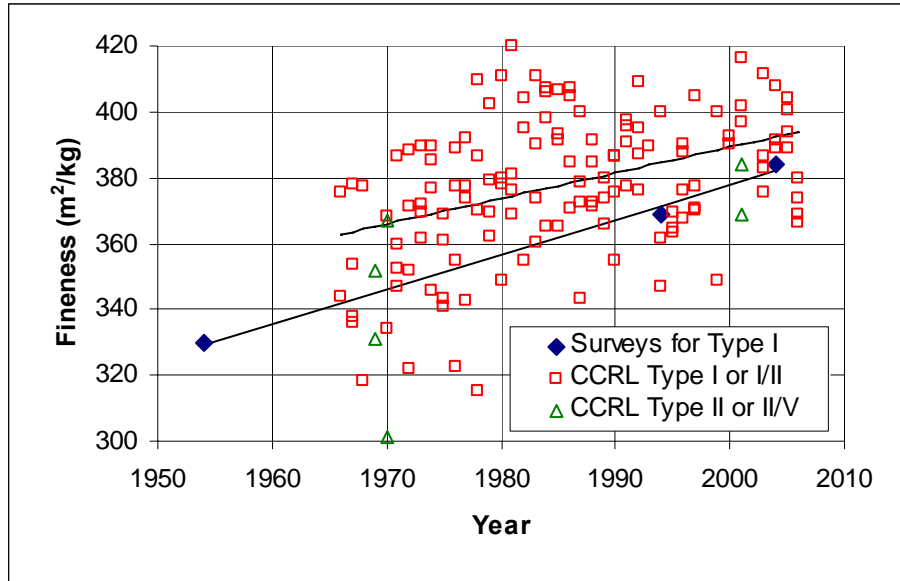


Figure 1. Changes in the Blaine fineness of cements from the 1950s to the present day. Regression lines are provided for the Type I survey and CCRL Type I or I/II data sets only.

In the early 1950s, Brewer and Burrows were perhaps the first to point out the critical linkage between cement fineness and concrete durability [3]. This point was reiterated by Houk et al. in the late 1960s when examining cements for use in the Dworshak Dam [4]. Burrows and others have continued this advocacy for the use of coarser cements in recent years [5-7], but as Figure 1 indicates, the trend continues much as before. The goal of this paper is to contrast a variety of early-age properties of a coarse vs. a fine cement for two cements that are currently readily available on the U.S. market, to provide a quantitative data set illustrating the influences of cement fineness on early-age performance.

Experimental

Two commonly used American Society for Testing and Materials (ASTM) Type I/II portland cements that differ widely in fineness were provided from two separate cement plants of the same manufacturer. Their measured oxide compositions, projected Bogue phase compositions, specific gravities, Blaine finenesses, and measured particle size distributions (via laser diffraction) are provided in Table I and Figure 2. While their chemical compositions are similar, with the exception of the coarser cement having a lower alkali content, their finenesses and particle size distributions are quite distinct. The finer cement has 25 μm as its modal value and basically contains no particles larger than 75 μm , while the coarser cement has 32 μm as its modal value and contains particles up to 120 μm in diameter.

To further isolate the influence of cement fineness, all experiments on cement paste and mortar specimens were conducted at a single value of water-to-cement ratio (w/c) of 0.35 by mass. This w/c was selected to be low enough to avoid any issues with bleeding and settlement of the cement particles, while still being in the range of values often utilized in concretes for high performance and paving applications. To enable proper placement and enhance workability, a

water-reducing admixture was used in preparation of the mortar mixtures and cement pastes evaluated for acoustic emission and restrained shrinkage performance, respectively. For measurements of calorimetry, chemical shrinkage and setting time, cement pastes with no chemical admixtures were prepared using a high shear blender, while mortars (strength, deformation and acoustic emission) were prepared according to the ASTM C305-99 procedures [8]. The mortar mixture proportions are provided in Table II. For measurements of restrained shrinkage (dual-ring tests), de-aired neat cement pastes with a water reducer (0.5 % by mass of cement) were prepared according to the procedure specified in [9].

Table I. Cement oxide compositions, Bogue potential phase mass fractions and fineness

Oxide or Property	Fine cement	Coarse cement
CaO	0.633	0.648
SiO ₂	0.203	0.209
Al ₂ O ₃	0.045	0.045
Fe ₂ O ₃	0.0339	0.041
SO ₃	0.0268	0.022
Na ₂ O	0.00077	0.003 (equiv.)
K ₂ O	0.00622	Not reported
MgO	0.0373	0.012
P ₂ O ₅	0.00127	Not reported
TiO ₂	0.00309	Not reported
Bogue - C ₄ AF	0.103	0.125
Bogue - C ₃ A	0.062	0.050
Bogue - C ₃ S	0.625	0.625
Bogue - C ₂ S	0.109	0.127
Specific gravity	3.22	3.21
Fineness (Blaine)	380 m ² /kg	311 m ² /kg
Median particle diameter	11.5 μm	17 μm

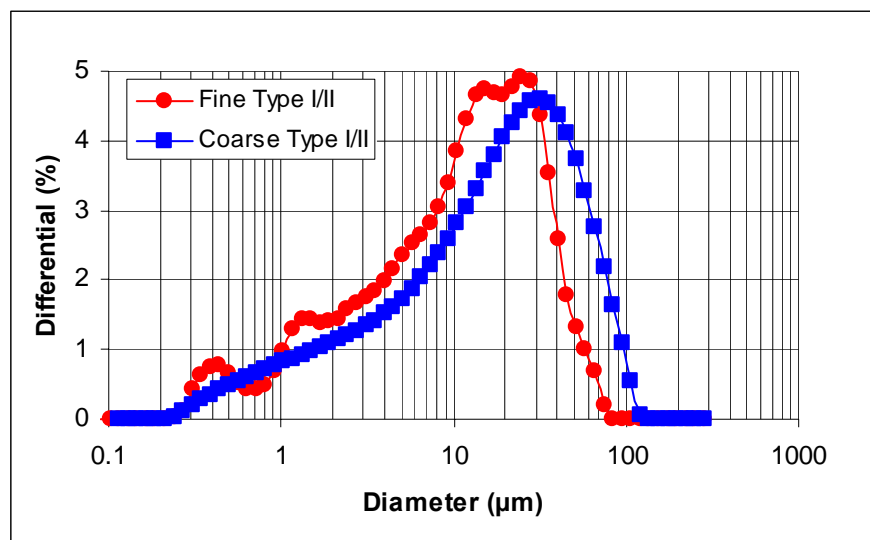


Figure 2. Measured differential particle size distributions for the two cements

Table II. Mortar mixture proportions used in the study

Material	Mixture Proportions (strength and autogenous deformation)	Mixture Proportions (acoustic emission)
Type I/II cement	1000.0 g	1000.0 g
Water	350.0 g	350.0 g
F95 fine sand ^A	522.5 g	---
Graded sand (ASTM C 778 ¹⁰)	397.1 g	1750.0 g
20-30 sand (ASTM C 778 ¹⁰)	397.1 g	---
GS16 coarse sand ^A	773.3 g	---
Water reducer	---	5.30 g

^AF95 and GS16 correspond to sand supplier designations.

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 5.25 g samples of pre-mixed cement pastes using a TAM Air Calorimeter²; to provide an indication of variability, two specimens were evaluated for each cement paste,
- 2) Semi-adiabatic calorimetry – the semi-adiabatic temperature rise was measured during the course of 3 d on single cement paste specimens with a mass of approximately 330 g using a custom-built semi-adiabatic calorimeter unit [11]; replicate specimens have indicated a standard deviation of 1.4 °C in the maximum specimen temperature achieved during a 3 d test,
- 3) Chemical shrinkage – measured during the course of 8 d or 12 d on triplicate $w/c = 0.35$ cement paste specimens, using the ASTM C 1608 standard test method [12]; according to the ASTM standard, the expected precision for the test is 0.0042 kg of water per kg of cement (lb of water per lb of cement),
- 4) Time of setting – measured on single cement paste specimens based on penetration of the Vicat needle according to ASTM C 191 [13]; in the standard, the single laboratory precisions are listed as 12 min and 20 min for initial and final time of setting, respectively,
- 5) Compressive strength – measured at 1 d, 3 d, 7 d, and 28 d on $w/c = 0.35$ mortar cube specimens, according to the procedures in ASTM C 109 [14], but with a loading rate of 20.7 MPa/min, switching to deformation control once a stress of 13.8 MPa was reached; three specimens were evaluated at each time, with the averages and standard deviations being provided in the results to follow,
- 6) Autogenous deformation – measured on duplicate mortar specimens sealed in corrugated tubes [15] (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,
- 7) Restrained shrinkage tests – measured on single specimens of each cement paste using a dual-ring configuration, with the specimens sealed for 5 d [16,17]; in ASTM C 1581 [18], the single laboratory repeatability standard deviation of the age at cracking is listed as 2 d, and,
- 8) Acoustic emission – measured on duplicate sealed mortar specimens using procedures described in detail previously [19,20].

² Certain commercial products are identified in this paper to specify the materials used and procedures employed. In no case does such identification imply endorsement by the National Institute of Standards and Technology, nor does it indicate that the products are necessarily the best available for the purpose.

At a constant w/c ratio, the initial three-dimensional microstructures based on these two cements will be vastly different. To illustrate this point, Figure 3 shows two-dimensional images from simulated three-dimensional starting microstructures [21] where the assumed spherical cement particle diameters follow the two distributions provided in Figure 2. Each two-dimensional image is $100\text{ }\mu\text{m}$ by $100\text{ }\mu\text{m}$. Clearly, the interparticle spacing (initial pore size) is much greater in the microstructure based on the coarser of the two cements. This interparticle spacing will have a large influence on the development of autogenous stresses and strains within the hydrating cement paste and mortar specimens [22]. In addition, the much larger surface area presented by the finer cement (Figure 3) should result in increased rates of hydration and internal energy (heat of hydration) production.

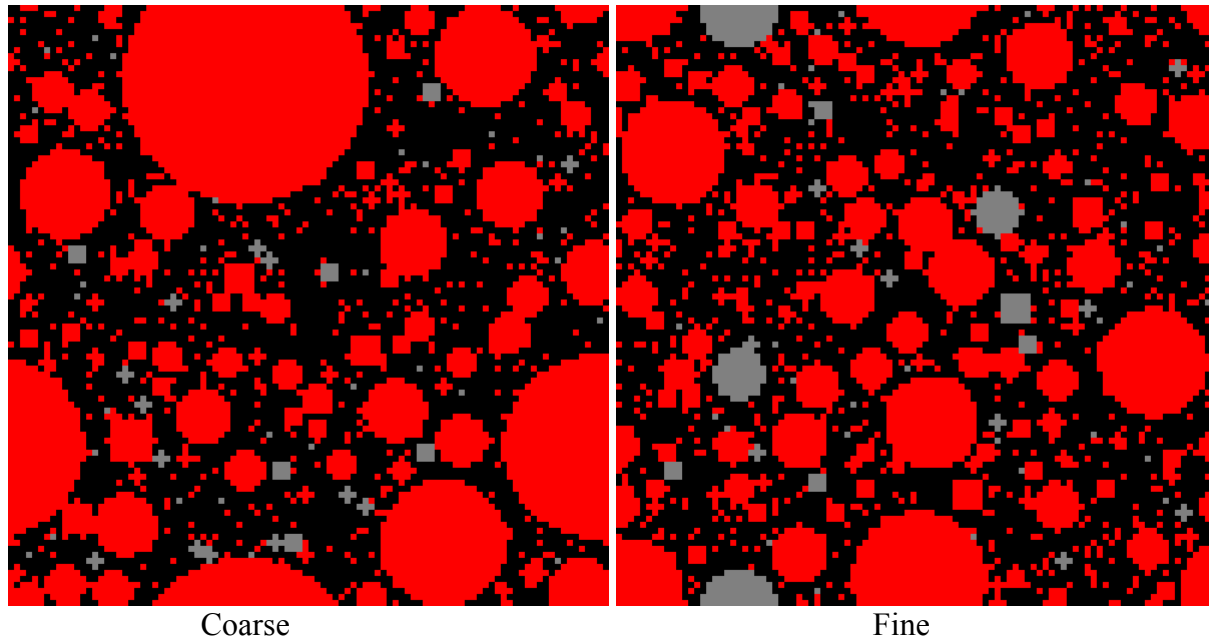


Figure 3. Single two-dimensional slice images ($100\text{ }\mu\text{m}$ by $100\text{ }\mu\text{m}$) from three-dimensional simulated starting microstructures for $w/c = 0.35$ cement pastes for the cements of two different finenesses (cement particles are red and gypsum particles are grey)

Results and Discussion

First, 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 finer cement consistently produces higher compressive strengths at all four testing ages. These increased compressive strengths at any given age are likely due to a combination of its increased reactivity and the smaller interparticle spacing exhibited in Figure 3. At an age of 1 d, the coarser cement achieves only about 50 % of the compressive strength of the finer one. By 28 d, however, it achieves 74 % of the strength exhibited by its finer counterpart. This exemplifies the general movement towards higher early-age strengths as the finer cement mortar achieves almost 50 % of its 28 d strength after just 1 d and over 70 % of its 28 d strength in just 3 d. For the coarser cement mortar, these corresponding values are only 32 % and 62 %, respectively. And

of course, a 28 d mortar cube compressive strength of 58 MPa, as exhibited by the coarser cement, would be sufficient for many construction applications.

Table III. Compressive strength results for $w/c = 0.35$ mortar cubes

Age	Compressive strength - fine (MPa)	Compressive strength - coarse (MPa)
1 d	36.2 (1.4) ^B	18.5 (1.2)
3 d	55.6 (2.4)	35.8 (3.1)
7 d	64.8 (1.0)	44.4 (2.4)
28 d	78.5 (2.2)	58.0 (3.5)

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

Two major contributions to early-age cracking of cement-based materials are thermal and autogenous stresses and deformations [23]. While the magnitudes of thermal stresses and strains will be highly influenced by the heat transfer conditions between the curing concrete and its environment, one key concrete material property is the energy generated within the concrete element due to the exothermic cement hydration reactions. Both isothermal and semi-adiabatic calorimetry can be used to provide valuable insights into these reactions. Isothermal calorimetry provides a measure of the reaction rate (heat released) at a constant temperature, while semi-adiabatic calorimetry provides a closer representation of actual field conditions where a portion of the energy released by the reactions will raise the temperature of the concrete, further increasing the reaction rates in an autocatalytic manner. It would generally be expected that a finer cement will have an increased heat release rate [24] and a corresponding larger temperature rise in a semi-adiabatic experiment, although the ultimate heat releases may be similar.

Isothermal calorimetry results for specimens tested at 25 °C for the two cements are provided in Figure 4. ASTM C 150 [25] specification limits on the 7 d heat of hydration for Type II (optional limit) and Type IV cements are also indicated in the figure. The coarser cement is seen to meet (falling below) the optional limit of 290 J/g cement for the 7 d heat of hydration for a Type II cement, while neither cement could be classified as a Type IV cement based on heat of hydration, as both exceed the Type IV 7 d limit of 250 J/g cement. To the authors' knowledge, few if any Type IV cements are currently produced in the U.S. In Figure 4, the variability between the two replicate specimens of each cement is seen to be minimal. Isothermal calorimetry experiments were also conducted at 10 °C and 40 °C to determine apparent activation energies for the two cements. For the finer cement, an activation energy of 37 kJ/mol was determined; the corresponding value for the coarser cement was 38 kJ/mol. Both of these are close to the value of 40 kJ/mol recommended as the default value by the ASTM C 1074 standard [26]. The higher heat release rate of the finer cement will generally lead to larger temperature rises within and larger temperature gradients through concrete elements, both of which can increase the risk of early-age cracking [23].

This increased temperature rise is further exemplified by Figure 5 that shows the semi-adiabatic temperature rise vs. time for equivalent cement pastes prepared with the two cements of different fineness. Initially, the temperature rise is fairly similar, but after about 4 h, the higher reaction rate of the finer cement results in an increased temperature rise (that further

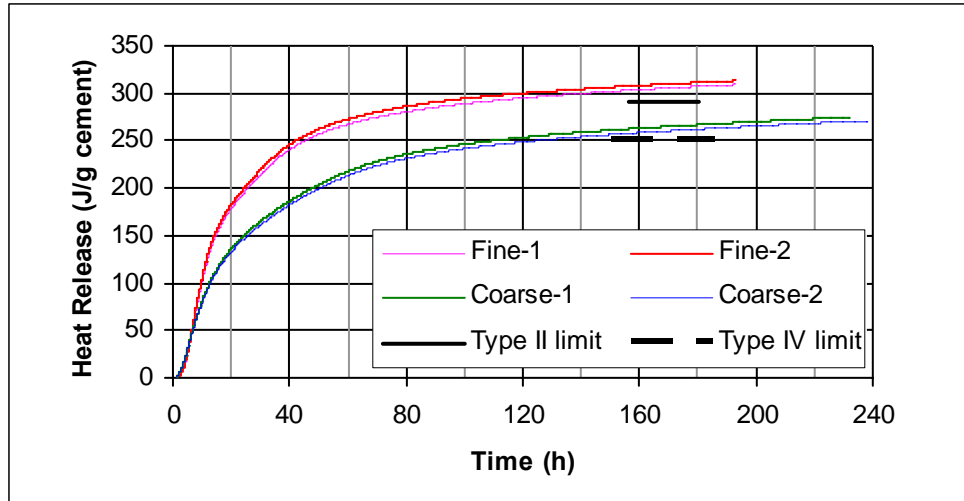


Figure 4. Isothermal calorimetry at 25 °C for replicate specimens of $w/c = 0.35$ pastes

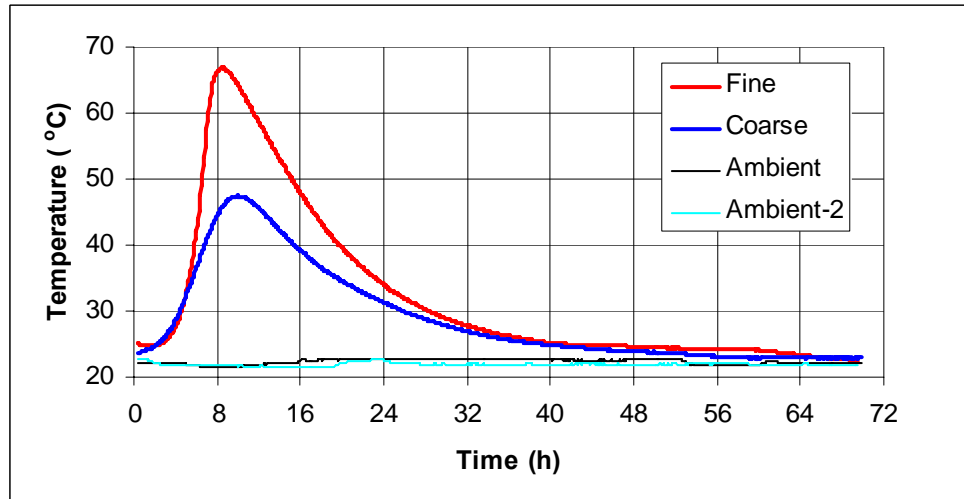


Figure 5. Semi-adiabatic temperature rise for $w/c = 0.35$ cement pastes

accelerates the cement hydration reactions). Eventually, much of the cement has reacted, such that the temperature rise can not be maintained and the heat losses to the environment in the semi-adiabatic experimental configuration begin to dominate over the heat produced by the hydration reactions. Thus, after the peak temperature is reached (with a peak rise of about 40 °C after 8 h for the finer cement and a peak rise of about 25 °C after 10 h for the coarser cement), the temperature gradually returns to ambient. In terms of thermal cracking, it is not only the maximum peak temperature achieved, but also the rate of this subsequent decrease that can contribute to early-age cracking [23]. Furthermore, as the specimen temperature exceeds 60 °C, hydration products such as (primary) ettringite may become unstable; then, the later precipitation of secondary ettringite sometime after subsequent cooling may present a serious durability concern [27]. For many concrete elements in many field environments, the “relatively extreme” temperature rises seen in Figure 5 would not be reproduced due to greater heat transfer between

the concrete and the environment. But, for large (mass) concrete structures, the temperature rises could be even more severe than those shown in Figure 5. For this reason, heat release has always been a major concern in dams and other large concrete structures [4]. In addition to coarser cements, other mitigation techniques such as the addition of slower reacting pozzolans, chilled aggregates, ice additions as part of the mixing water, and the use of cooling pipes have been employed.

The setting characteristics of the cement pastes were characterized based on Vicat needle penetration measurements. The results are presented in Figure 6, along with the early-age isothermal calorimetry curves. Rather surprisingly, the coarser cement exhibits an earlier setting time as it exhibits an early-age reactivity that is greater than that of the finer cement, as illustrated by the heat release curve in Figure 6. The two heat of hydration curves later cross one another at 7 h and beyond that point, as shown in Figure 4, the finer cement proceeds to release more heat than the coarser one. Considering that degree of hydration should be proportional to heat release [21], a careful examination of Figure 6 also reveals that the coarser cement is requiring slightly less hydration to achieve equivalent “set” (Vicat needle penetration) than the finer cement, in agreement with previous predictions based on three-dimensional microstructure modeling [24].

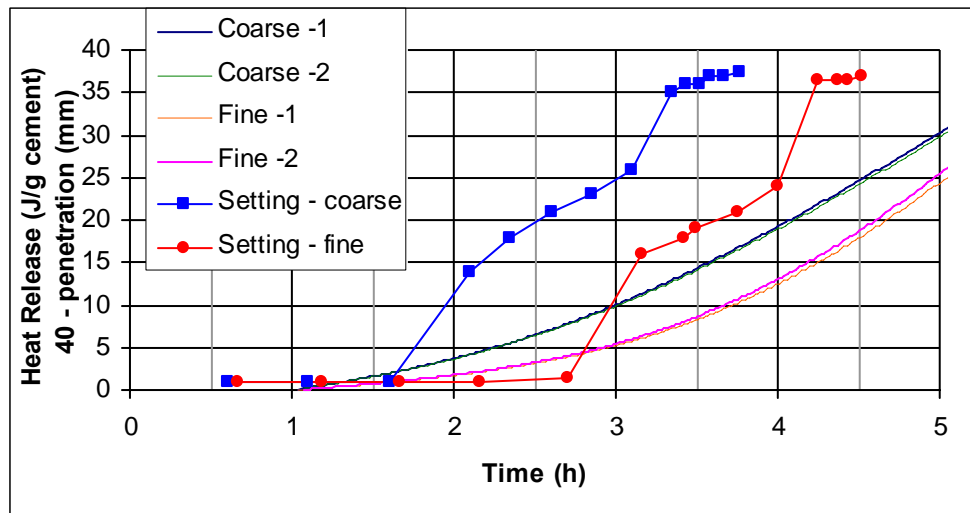


Figure 6. Vicat setting (plotted as 40 - needle penetration) and heat release for $w/c = 0.35$ cement pastes

Another measure of early-age hydration rates can be provided by chemical shrinkage measurements [12,28,29]. While the ASTM test method [12] specifies a w/c ratio of 0.4 in order to minimize both bleeding and depercolation effects, here measurements were performed on pastes with $w/c = 0.35$ to be consistent with the other measurements performed in this study. The results, provided in Figure 7, once again indicate the enhanced reactivity of the finer cement relative to the coarser one. It is quite interesting to also note that the coarser cement just meets the requirement of having a 12 h chemical shrinkage less than or equal to 0.0105 mL/g cement, as suggested previously by Burrows et al. [7] for producing a crack resistant cement.

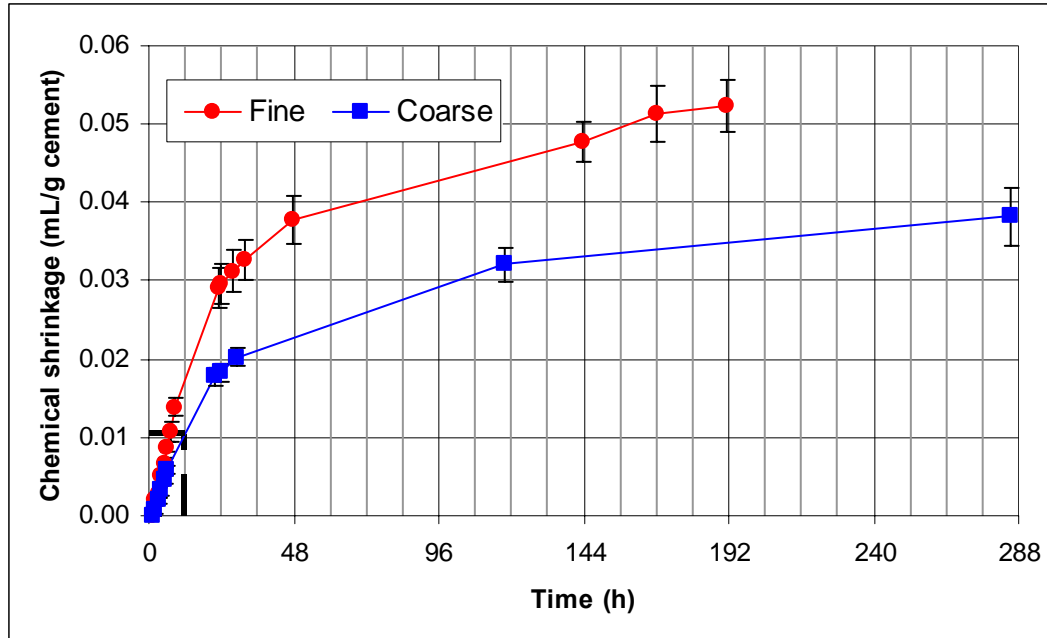


Figure 7. Chemical shrinkage at 25 °C for $w/c = 0.35$ cement pastes. Error bars represent one standard deviation determined based on three replicate specimens for each cement. Dashed heavy lines indicate the 12 h limit set by Burrows et al. [7] for a low crack cement

In Figure 8, it is demonstrated that the hydration rates as measured by chemical shrinkage or heat of hydration for these two particular cements are equivalent within a scaling factor. In 1935, Powers determined this scaling factor to convert from chemical shrinkage to heat release to be $80.8 \text{ (J/g)/(g water/100 g cement)}$, for four different cements of that era [28]. More recently [21], scaling factors of $70.7 \text{ (J/g)/(g water/100 g cement)}$ and $86.2 \text{ (J/g)/(g water/100 g cement)}$ have been determined for CCRL proficiency cements 115 and 116 [1], respectively. For the results presented in Figure 8, we find scaling factors of $66.5 \text{ (J/g)/(g water/100 g cement)}$ and $77.8 \text{ (J/g)/(g water/100 g cement)}$ for the finer and coarser cements, respectively, in reasonable agreement with the previously determined values.

In addition to providing a convenient measure of early-age hydration rates, chemical shrinkage measurements also provide an indication of the volume of empty porosity that will be created in a cement-based material cured under sealed conditions. As such, it is one of the key determinations in properly proportioning a concrete mixture to incorporate internal curing, for example [30]. The results in Figure 7 would indicate that the creation of empty porosity, namely self-desiccation, will be more severe at early ages in the finer cement paste. In addition to the volume of empty porosity being created, the sizes of the pores being emptied (according to the Kelvin-Laplace equation) also greatly influences the development of autogenous stresses and strains in these materials [22]. Figure 3 would suggest that smaller pores will be emptied in the finer cement systems. With both an enhanced self-desiccation and the emptying of smaller pores, the autogenous shrinkage of a mortar made with the finer cement should be much greater than that of one containing the coarser cement.

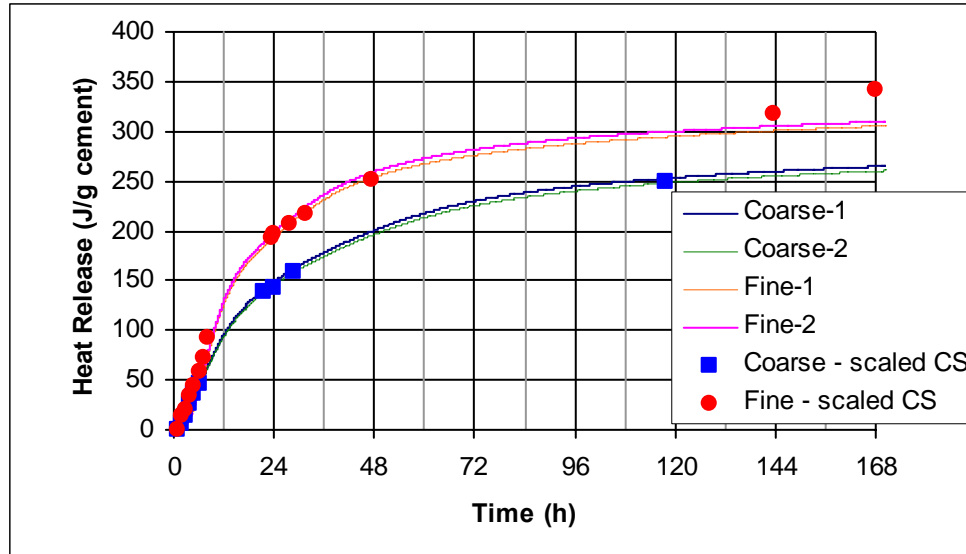


Figure 8. Scaled chemical shrinkage (CS) along with heat of hydration for the two cements. Scaling factors utilized for chemical shrinkage are provided in the text

As shown in Figure 9, this is indeed the case. In fact, the coarser cement mortar actually exhibits a net autogenous expansion at 28 d, as has been observed previously for $w/c = 0.35$ cement pastes based on cements with Blaine finenesses of $212 \text{ m}^2/\text{kg}$ and $254 \text{ m}^2/\text{kg}$ [21]. In that study, cement pastes made using cements with Blaine finenesses of $387 \text{ m}^2/\text{kg}$ and $643 \text{ m}^2/\text{kg}$ both exhibited autogenous shrinkages of more than -500 microstrain. The microstrains measured for the mortar based on the finer cement in this study are lower than this due to the dilution factor (less shrinking cement paste per unit volume in a mortar vs. a paste), the internal restraint offered by the sand particles, and possibly a reduction in autogenous stresses resulting from the presence of larger pores in the interfacial transition zones between cement paste and sand particles [24,31].

The exact cause of the expansion in the case of the coarser cement is unknown, but it is commonly conjectured to be due to either ettringite formation or local water imbibition and swelling of the cement hydration products [22]. This same expansion would be present in the finer cement system, but, in that case, would simply be overwhelmed by the autogenous shrinkage. Thus, the autogenous deformation plotted in Figure 9 is the sum of (at least) two competing effects and which one dominates depends not only on the cement fineness [22], but also on the w/c ratio [32,33]. For each cement having a given degree of fineness, there will be a critical w/c below which the measured autogenous deformation will exhibit a net shrinkage and above which a net expansion will be measured [32,33].

Figure 10 shows residual stress development in coarse and fine cement pastes assessed using a dual ring, restrained shrinkage test. As seen in the figure, the fine cement shows no stress development until 11 h after which time the measured residual stresses begin to increase. This is similar to the evolution of free shrinkage experienced by the specimen over this time (Figure 9). A peak residual stress (tensile) of 2.45 MPa develops in the ring specimen at 87 h, and a visible crack appears, as the residual stress developed has exceeded the strength (tensile) of

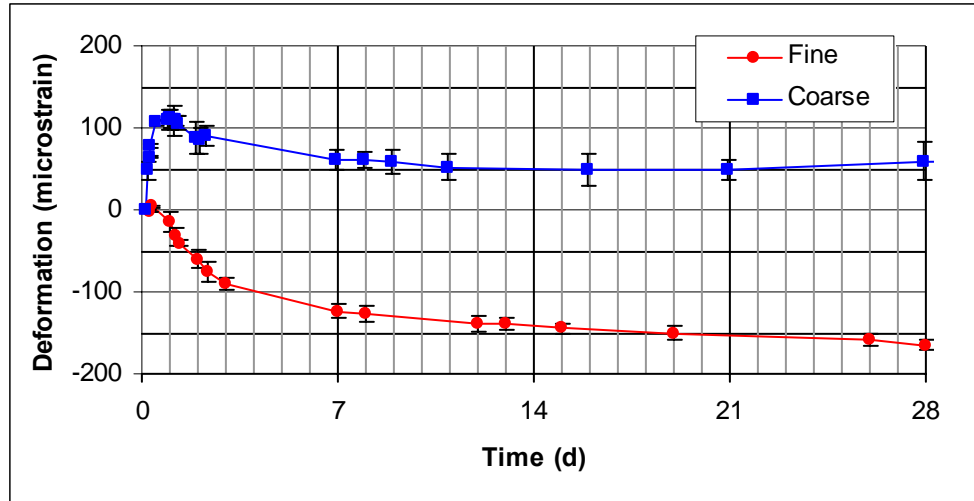


Figure 9. Autogenous deformation of $w/c = 0.35$ mortars cured under sealed conditions at 25 °C. Error bars represent one standard deviation determined based on two replicate specimens for each mortar

the specimen. The coarse cement specimen shows no development of residual stresses, until 6.5 h after which time a compressive stress begins to develop in the specimen. This is in agreement with the earlier set time (Figure 6), and autogenous expansion measured for this cement (Figure 9). A peak compressive stress of 0.9 MPa is observed to develop in this specimen at 29 h. After this time, the magnitude of the compressive stress developed is observed to consistently decrease, until an age of 61 h, when the development of net tensile stresses initiates in the specimen. A peak tensile stress of 0.9 MPa develops in the coarse cement mortar at a specimen age of 120 h, when the test was terminated. No cracking was observed in the coarse cement system during the course of the test. Consequently, even though coarse cements develop a lower strength as compared to fine cements (Table III), coarse cement systems may exhibit a decreased risk of cracking at early ages, due to their decreased autogenous shrinkage.

To quantify damage development (microcracking) in the cement mortars, the acoustic energy release was recorded. Acoustic energy is defined as the cumulative area under the voltage versus time response for each acoustic event; and provides quantifiable information that can be related to the mechanical fracture energy of cementitious composites [34]. Figure 11 shows the cumulative acoustic energy measured for the coarse and fine cement mortars. Soon after the time of initiation of the test (at 18 h), a rapid increase (and divergence) in acoustic energy is observed in the fine cement mortar. After this time the acoustic energy recorded in the fine and coarse mortar is observed to increase, although at a higher rate for the fine cement system. In addition, the acoustic energy released by the fine cement mortar is observed to be consistently higher than that of the coarse cement mortar. This can be explained by the higher autogenous shrinkage experienced by the fine mortar (Figure 9), which would promote significant microcracking at the paste-aggregate interfaces [35]. These results would indicate lower damage development and less expended fracture energy in coarse cement systems, which would contribute to a lower risk of early-age cracking.

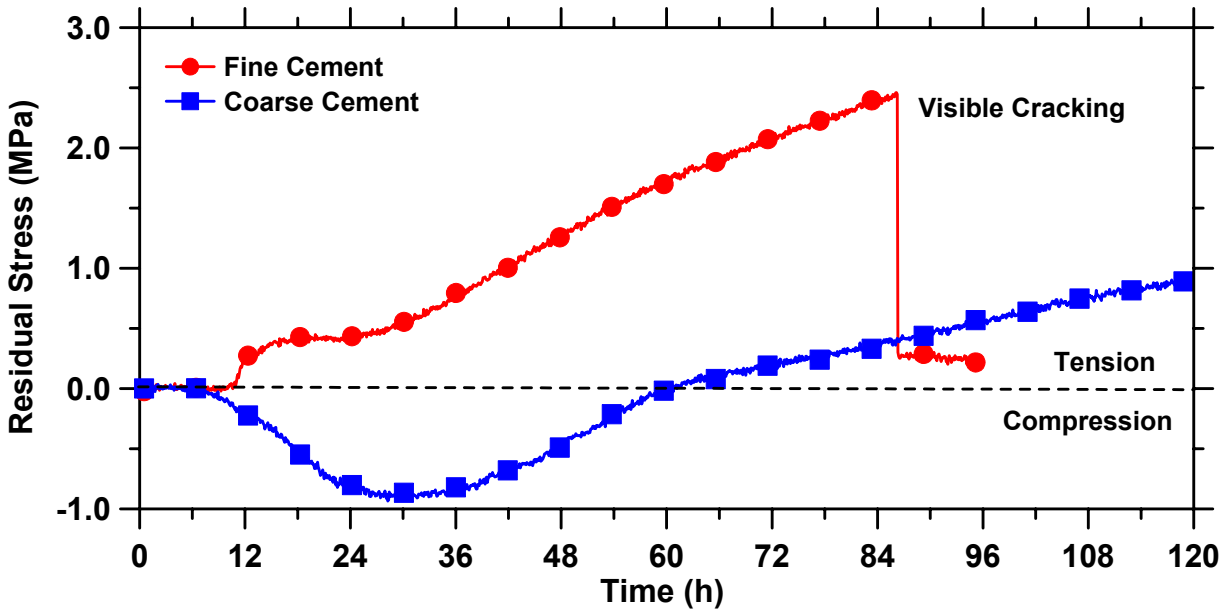


Figure 10. Residual stress development as a function of time for $w/c = 0.35$ coarse and fine cement pastes cured under sealed conditions at 23 °C

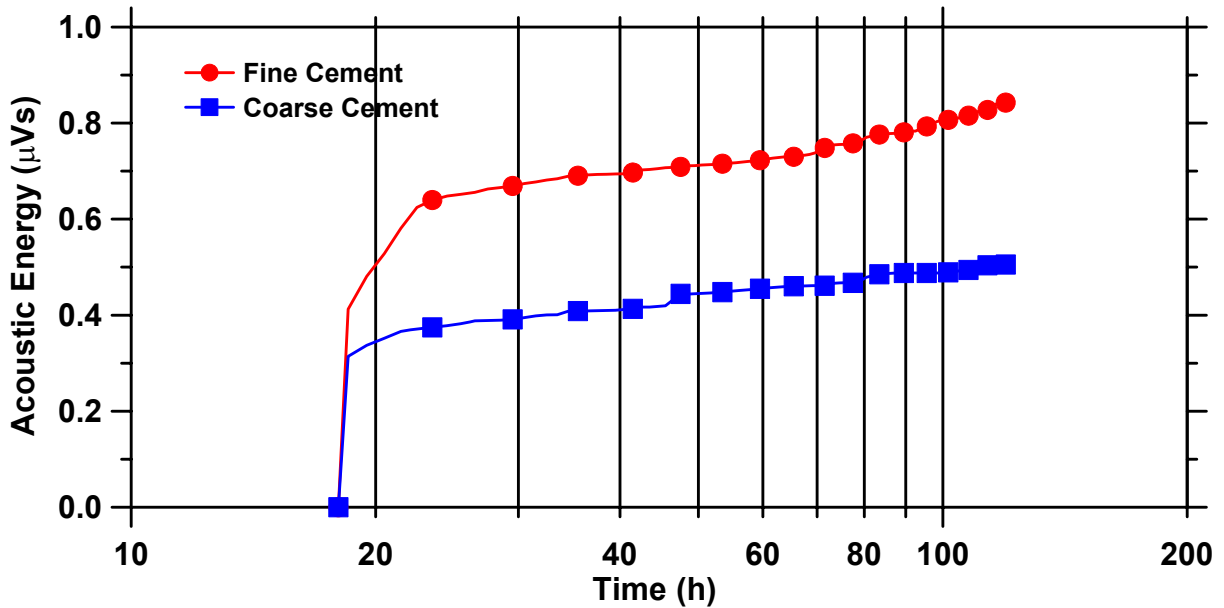


Figure 11. Cumulative acoustic energy as a function of time for $w/c = 0.35$ coarse and fine cement mortars cured under sealed conditions at 23 °C

Conclusions

Comprehensive studies of a variety of early-age properties of coarse and fine cement pastes and mortars have indicated that:

- Chemical shrinkage and heat of hydration are both valid indicators of early-age hydration.

- While the coarser cement exhibits compressive strengths well below those of the finer cement at all ages tested, it also releases less heat and results in a substantially lower semi-adiabatic temperature rise.
- The coarse cement system initially develops a compressive stress, exhibiting lower residual stress development and a lower risk of cracking at early ages as compared to the fine cement system. This is primarily due to a lower magnitude of autogenous deformation experienced by these (coarse cement) systems, contributing to a decrease in autogenous stresses (due to shrinkage and internal relative humidity change) developed in coarse cement systems.
- As exemplified by the results of this study, high early-age strength cements will generally increase both the thermal and autogenous deformation contributions to early-age cracking.

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