

# A review of early-age properties of cement-based materials

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## Abstract

This paper provides an overview of the early-age properties of cement-based materials, from a materials science perspective. The major physical and chemical processes occurring at early ages are reviewed and strategies for mitigating early-age cracking are presented. Published by Elsevier Ltd.

**Keywords:** Curing; Drying; Early-age cracking (nominated); Hydration; Shrinking

## 1. Settling, bleeding, and evaporative water loss during early-age curing/drying

Immediately after placement, gravitational forces and the local drying environment begin to influence the (micro)structure of a cement paste, mortar, or concrete. Depending on the mixture's water-to-cementitious materials mass ratio ( $w/c$ ) (and aggregate volume fraction), the initial freshly cast material may be thought of either as a concentrated suspension of rigid particles in water or as a granular water-filled porous media. In the former case, significant settling will be expected to occur, accompanied by bleeding. For present-day Portland cement pastes without admixture additions, for example, measurable bleeding and settling are generally observed for water-to-cement ratios ( $w/c$ )  $> 0.4$ . As the solid particles settle and a corresponding volume of water rises to the top of the specimen, a microstructural (porosity/density) gradient will be established through the thickness of the specimen. In addition to the concentration and particle size distribution (PSD) of the solids, the details of this gradient will depend also on the evaporative water loss from the specimen's top surface, e.g., the drying conditions.

X-ray absorption measurements have been previously applied to examining these microstructural gradients for cement pastes cured under sealed and drying conditions [1]. In the former case, as particles settle, the volume fraction of particles

as a function of depth assumes a fairly linear profile (with significant local variations) varying from a higher concentration of particles at the bottom of the specimen to a lower concentration at the top. This is illustrated in Fig. 1 that provides measured X-ray transmission profiles for a  $w/c=0.40$  blended cement paste achieved after 2.5 h and 4.5 h of sealed curing. A lower transmission of the X-ray signal (lower normalized counts, where the counts transmitted have been normalized by the counts transmitted through a reference specimen) indicates a higher concentration of particles, as the cement particles have a much higher X-ray absorption coefficient than water. In this case, the lower concentrations of solids (higher water-filled porosity) established at the top surface during the first few hours of sealed curing may persist throughout the life of the material, resulting in a surface layer that is weaker and that may be much more susceptible to scaling phenomena, for example.

The situation is further complicated when drying (water evaporation) is also occurring at the top surface of the specimen. If the rate of evaporative water loss is even slightly greater than the rate of bleeding, menisci will be created between the particles at the top of the specimen, creating a capillary tension in the water according to the Kelvin–Laplace equation:

$$\sigma_{\text{cap}} = \frac{2\gamma\cos\alpha}{r} = \frac{-\ln(RH)RT}{V_m} \quad (1)$$

where  $\sigma_{\text{cap}}$  is the capillary tension (Pa),  $\gamma$  is the surface tension of the pore solution (N/m),  $\alpha$  is the contact angle between the pore solution and the capillary pore walls,  $V_m$  is the pore

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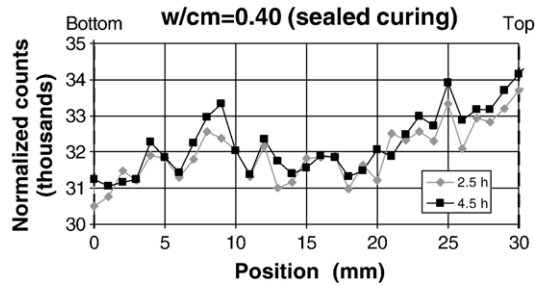


Fig. 1. Normalized counts for X-rays transmitted through a  $w/c=0.40$  blended cement paste cured under sealed conditions at 23 °C, as a function of curing time (2.5 h or 4.5 h) and depth [2]. Top of specimen is located at 30 mm.

solution molar volume ( $\text{m}^3/\text{mol}$ ),  $r$  is the meniscus radius (m), RH is the relative humidity (with values between 0 and 1),  $R$  is the universal gas constant [ $8.314 \text{ J}/(\text{mol K})$ ], and  $T$  is the absolute temperature in K. In Eq. (1), often a contact angle of  $0^\circ$  (complete wetting of the pore walls by the liquid) is assumed. This capillary tension will compress the granular porous media, particularly near the top surface. In this case, in addition to the densification occurring at the bottom of the specimen during settling/bleeding, significant local densification may also occur near the top surface of the specimen, as illustrated by the X-ray transmission results shown in Fig. 2, for a  $w/c=0.45$  cement paste immediately exposed to drying conditions. In comparing the 0.67 h and 4.67 h normalized counts profiles in Fig. 2, one can readily observe that a preferential densification has occurred at the top (exposed) surface. From this perspective, the American Concrete Institute (ACI) recommended practice of applying a curing compound only when the top surface of the concrete first appears “dry and free of surface water” [4] should also be beneficial in promoting the formation of a superior quality surface layer in the field concrete. The development of this capillary tension can also be responsible for plastic shrinkage cracking of cement-based materials. This cracking will be dependent on the rate of evaporation, the initial water content of the mixture, and the surface tension of the pore solution [5].

Concurrent with settling/bleeding/evaporation, some small but significant hydration of the cement will be taking place during the first few hours of curing. The general influence of this hydration will be to hasten the transition of the material from a suspension of rigid particles in solution to a “granular” porous solid, by locally (and ultimately globally) connecting particles together into agglomerates. However, any reductions in capillary pore sizes (that would result in increased capillary pressures) due to this small amount of hydration are likely to be overwhelmed by the pore size reductions due to settling and local particle rearrangement, at these very early stages in the curing process. These hydration reactions will also result in a reduction in total volume of the system due to the chemical shrinkage accompanying them; this topic will be considered in detail in the sections that follow.

X-ray absorption measurements have also been applied to observing the water distribution in cement pastes during further drying/hydration, after the initial settlement [2,3,6]. In general,

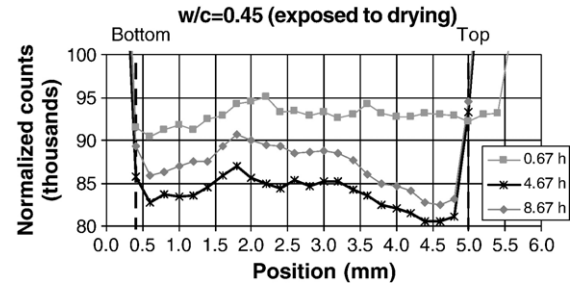


Fig. 2. Normalized counts for X-rays transmitted through a  $w/c=0.45$  Portland cement paste immediately exposed to drying conditions (23 °C and 50% RH), as a function of curing time (0.67 h, 4.67 h or 8.67 h) and depth [3]. Top of specimen is located at about 5 mm.

drying is observed to occur fairly uniformly throughout the thickness of the specimen, and not as a front that penetrates from the exposed surface inward. In this respect, the drying of cement pastes and mortars seems to more closely follow the theory presented previously for the convective drying of a porous medium [7] than that developed for the drying of gels [8]. Typical results are provided in Fig. 3 that shows the X-ray transmission profiles for a  $w/c=0.45$  cement paste immediately exposed to a drying environment.

Similar to previous observations made on non-reactive bead packs [9], in bilayer composites, water is always first observed to be removed from a coarser pore structure during the initial stages of drying/hydration before subsequently being removed from the finer one [6]. This is true whether the coarser pore structure is due to a higher  $w/c$  ratio or to the use of a cement with a coarser PSD (at a constant  $w/c$ ) [6]. The effects of a shrinkage-reducing admixture (SRA) on this drying process are quite significant [5,10], but will be discussed in a separate section later in this paper.

## 2. Cement hydration and early-age properties

It is the hydration of cement(itious materials) that is responsible for the transformation of concrete from a viscous suspension to a rigid load-bearing and durable solid element. In this paper, hydration will be considered specifically in terms of physical/microstructural, thermal, and moisture (saturation) effects. The influences of mixture parameters such as  $w/c$  and

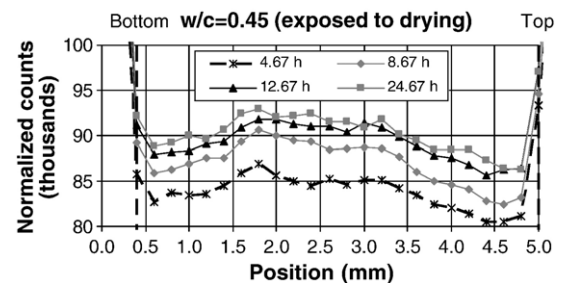


Fig. 3. Normalized counts for X-rays transmitted through a  $w/c=0.45$  Portland cement paste immediately exposed to drying conditions (23 °C and 50% RH), as a function of curing time (4.67 h, 8.67 h, 12.67 h, or 24.67 h) and depth [3]. Top of specimen is located at about 5 mm.

cement PSD on the magnitudes of these effects will also be presented.

## 2.1. Physical/microstructural effects

### 2.1.1. Setting

The setting of cement is a percolation process in which isolated or weakly bound particles are connected together (percolated) by the formation of hydration products [11,12]. Initial and final setting, via Vicat measurements for example, are generally defined by when the microstructure presents some finite mechanical resistance to penetration or shear. Three previous studies have shown a quantitative relationship between measured Vicat needle penetrations and solids percolation as estimated using a three-dimensional microstructural model [13–15]. This equivalence is further illustrated in Fig. 4 that compares needle resistance (determined as  $40 - \text{the measured needle penetration in mm}$ ) to the volume fraction of percolated solids for the same cement used to prepare pastes with four different  $w/c$  [16]. These results also illustrate the strong influence of  $w/c$  on setting, as higher  $w/c$  pastes will require more hydration (and likely more time) to achieve set due to the larger initial particle spacing. On the other hand, at a constant  $w/c$ , the influence of cement PSD on setting is not as obvious. While a coarser cement may require more time to achieve set due to its slower hydration rate, it can actually achieve set at a lower degree of hydration as fewer “bridges” need to be built between particles when fewer (but larger) particles are present in the initial paste [17].

### 2.1.2. Early-age mechanical property development

Concurrent with the development of a percolated solids network is the genesis of measurable solid mechanical prop-

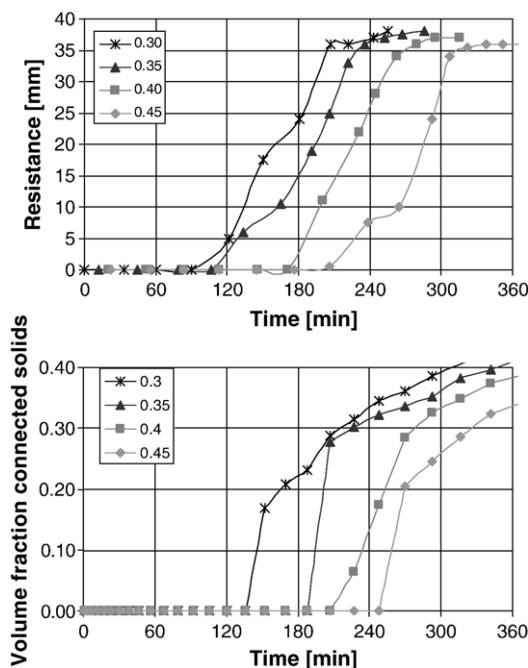


Fig. 4. Two “views” of the setting process in cement paste as a function of time and  $w/c$ : needle resistance (top) and connected solids volume fraction from the CEMHYD3D computer model (bottom) [16].

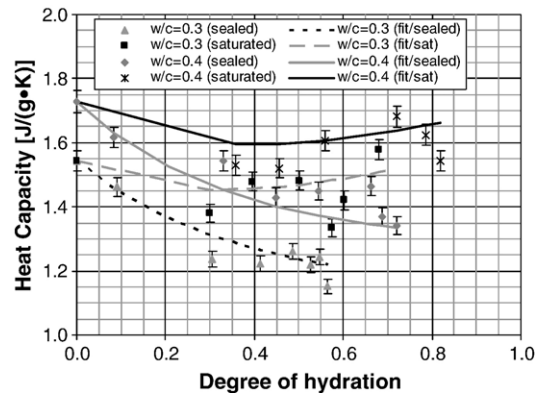


Fig. 5. Measured and fitted heat capacities of hydrating cement paste as a function of degree of hydration, with  $w/c=0.3$  and  $w/c=0.4$ , cured under saturated or sealed conditions at 20 °C [22]. Error bars indicate a reproducibility of  $\pm 2\%$  in the experimental measurements.

erties including elastic modulus, strength, stress relaxation, and creep. The same ultrasonic measurements that can be used as an indicator of setting [12] have also been extended to predict compressive strength gains at early ages [18]. In general, these mechanical properties are much more difficult to measure at early ages than later in the hydration process, as they are often continuously changing during the course of the physical measurement. Measurement of stress relaxation and creep in tension are particularly challenging, but progress is being made [19]. In compression, conventional creep loading has typically been employed [20]. Understanding the development of these mechanical properties at early ages is one key to a fundamental materials science-based prediction of early-age cracking, as they control the resistance half of the load/resistance paradigm [20,21].

## 2.2. Thermal effects

Assuming proper curing and thus neglecting evaporation, one of the two major causes of early-age cracking is thermal effects, the other being autogenous shrinkage. Depending on the environmental exposure, a concrete will typically first heat up and expand due to heat produced during early-age cement hydration. If the subsequent cooling is too rapid, the concrete may crack, particularly if locally or globally restrained. To properly understand the contribution of these thermal effects to early-age cracking, a quantitative characterization of the concrete’s thermophysical properties, its heat of hydration, and its interaction with the environment are all of critical importance.

### 2.2.1. Thermophysical property development — heat capacity, thermal conductivity, and coefficient of thermal expansion

Because the hydration of Portland cement significantly alters the volume fractions and spatial arrangement of solids, liquids, and gases (air voids and empty capillary pores) within the three-dimensional microstructure, it would be expected that the thermophysical properties of cement paste such as heat capacity, thermal conductivity, and coefficient of thermal

expansion would vary with hydration. As shown in Fig. 5, the heat capacity of cement paste is a strong function of both  $w/c$  and curing conditions [22]. This is mainly due to the high heat capacity of water (4.18 J/(g K) vs. about 0.75 J/(g K) for dry cement powder) and its decrease as water is (chemically and physically) bound into hydration products. More water (higher  $w/c$ ) results in a higher heat capacity as does saturated curing (with its accompanying water imbibition) relative to sealed curing.

As shown in Fig. 6, within the experimental error of the measurement, the thermal conductivity of hydrating cement pastes is basically a constant value of 1.0 W/(m K), for the two values of  $w/c$  and the two curing conditions used [22]. The thermal conductivities of the starting materials (water: 0.604 (W/m K) and cement: 1.55 W/(m K) at 20 °C) and those of the hydration products are apparently close enough to one another that as solid and liquid pathways are percolated, depercolated, and repercolated during the course of hydration and aging, the thermal conductivity remains essentially unchanged (e.g., within  $\pm 10\%$ ). This can be contrasted against electrical conductivity and ionic diffusivity, which both change dramatically during the course of hydration [15,23].

Equally important to predicting early-age thermal cracking is an accurate characterization of the concrete's coefficient of thermal expansion. This property is particularly difficult to measure at early ages due to the confounding influences of the ongoing hydration, etc. [24]. Fiber optic-based techniques may offer an in situ non-destructive solution to this dilemma [25]. Values of  $10 \times 10^{-6}$  [1/K] to  $12 \times 10^{-6}$  [1/K] are typically employed for concrete.

### 2.2.2. Heat of hydration

As cement hydrates, a significant amount of energy is released as heat. This heat of hydration must be included in any early-age model of heat transfer in a concrete. The heat released is dependent on the phase composition of the cement; literature values for the various cement clinker phases are compiled in Table 1 [26,27]. In blended cements, the mass-normalized heat release can be either increased or decreased depending on the mineral admixture employed. For example, silica fume has a heat of hydration (when reacting pozzolanically with  $\text{Ca}(\text{OH})_2$ ) of about 780 kJ/kg fume [28], while the reactions of fly ash and slag typically produce less heat than those of Portland cement.

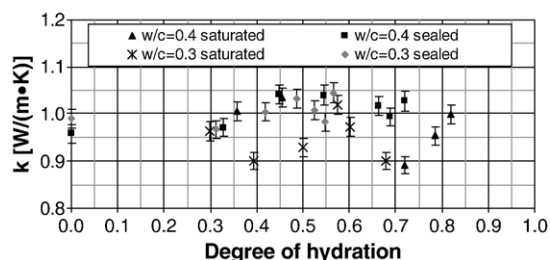


Fig. 6. Measured thermal conductivity of hydrating cement paste as a function of degree of hydration, with  $w/c=0.3$  and  $w/c=0.4$ , cured under saturated or sealed conditions at 20 °C [22]. Error bars indicate a reproducibility of  $\pm 2\%$  in the experimental measurements.

Table 1

Enthalpies of complete hydration for major phases of Portland cement

Phase	Enthalpy (kJ/kg phase)
$\text{C}_3\text{S}$	517
$\text{C}_2\text{S}$	262
$\text{C}_3\text{A}$	908, 1672, 1144 <sup>a</sup>
$\text{C}_4\text{AF}$	418, 725 <sup>a</sup>

<sup>a</sup> For  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$  hydration, values are for conversion to  $\text{C}_3\text{AH}_6$ , ettringite, and monosulfate (AFm) phase (only for  $\text{C}_3\text{A}$ ), respectively.

Heat of hydration is typically measured using a standardized heat of solution technique [29] or semi-adiabatic methods; a new standard method based on isothermal calorimetry has been developed in the Nordic countries [30] and is now being considered by the American Society for Testing and Materials (ASTM) C01.26 Heat of hydration subcommittee. In addition, virtual test methods for heat of hydration of ordinary Portland cement are also under development within ASTM [31].

### 2.2.3. Environmental factors at early ages

A number of computer models have been developed and are either commercially or freely available for predicting the temperature and stress/strain response of concrete exposed to a variable environment at early ages [28,32–37]. In addition to a quantitative understanding of the properties of concrete discussed above and in the following section, accurate predictions by such models are requisite on having a detailed quantitative characterization of the exposure environment, including temperature, relative humidity, wind speed, and solar radiation, and the applied curing conditions (curing membrane, water misting, etc.) [37]. While further research in these latter areas is clearly needed, the models have been used successfully in many cases over the past decade.

## 2.3. Moisture effects

### 2.3.1. Chemical shrinkage

As cement hydrates, the volume of the hydration products is less than that of the starting materials (including water). This chemical shrinkage has major implications for the early-age performance of cement-based materials, as will be discussed in detail in the sections that follow. Powers was the first to quantify the chemical shrinkage (water imbibition) of the various cement clinker phases in 1935 [38]. An experimental technique for

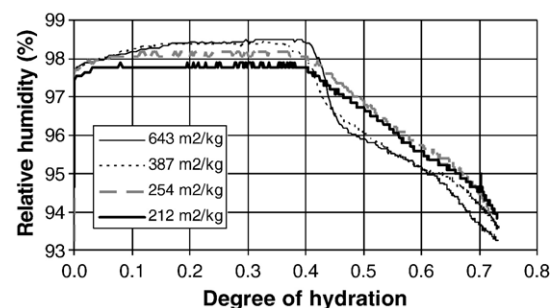


Fig. 7. Internal relative humidity vs. degree of hydration as a function of cement fineness for cement pastes prepared with  $w/c=0.35$  and cured under sealed conditions at 30 °C [54].



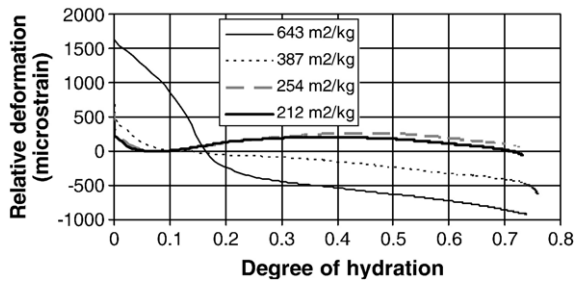


Fig. 8. Autogenous deformation vs. degree of hydration as a function of cement fineness for cement pastes with  $w/c=0.35$ , cured at 30 °C [54]. Deformation values have been zeroed at the setting time (degree of hydration) of each cement paste.

quantifying chemical shrinkage that was studied in detail by Geiker [39] has recently been approved as ASTM Standard Test Method C1608 [40]. It is based on measuring the volume of water imbibed into a cement paste (or mortar) sample of known mass during hydration under isothermal saturated conditions. A similar technique has been standardized in Japan [41]. Due to the depercolation of the capillary porosity that may occur during hydration and limit this water transport [42,43], both the specimen thickness and the  $w/c$  must be within a limited range (nominally a few millimeters and 0.4, respectively) to obtain meaningful results at later ages.

Chemical shrinkage can also be computed by assuming a set of cement hydration reactions and molar volumes for each cement component. This approach has been used by numerous authors [44–46] with variable agreement between their published values. In general, though, the chemical shrinkages of the aluminate phases ( $C_3A$  and  $C_4AF$ ) are about 50% higher (on a per unit mass basis) than those of the calcium silicates (which are about 0.07 mL/g  $C_nS$ ). The chemical shrinkage of silica fume during its pozzolanic reaction with  $Ca(OH)_2$  is particularly high, being on the order of 0.22 mL/g silica fume [47]. The ultimate chemical shrinkage of a typical hydrating Portland cement paste can be on the order of 10% by volume.

### 2.3.2. Self-desiccation

When cured under sealed, partially saturated conditions, or saturated conditions but where depercolation of the capillary porosity has already occurred, chemical shrinkage can lead to the creation of empty porosity and a reduction in the internal RH, a process known as self-desiccation. In general, the largest pores within the cement paste microstructure will empty first during self-desiccation [44,48]. As shown in Eq. (1), the menisci formed in these (partially) empty pores will create a capillary tension within the pore solution and also reduce the internal RH of the specimen. This self-desiccation process is thus largely responsible for the autogenous shrinkage of cement-based materials that has come to the forefront in recent years due to field problems with early-age cracking, particularly of high-performance concretes (HPC). Self-desiccation is not always detrimental, however, as it can be used to advantage in accelerating the drying of concrete floors prior to the application of carpeting and other coverings and may also increase the frost

resistance of early-age concrete. It has been the topic of a continuing series of international seminars, starting in 1997 [49].

### 2.3.3. Internal relative humidity

As indicated above, measurement of the internal RH of cement-based materials can provide valuable insight into their internal stresses. Experimental methods have been developed both for laboratory measurements [50] and more recently for field use [51], but only a few data from actual field exposures have been published to date [52]. The reduction in internal RH will also reduce the hydration rates of the remaining cement clinker phases [44,53]. This internal RH reduction will be significantly less in systems with higher  $w/c$  due to the initially larger spacing between cement particles (larger pores). At a constant  $w/c$  and the same degree of hydration, the RH reduction at later ages (degree of hydration  $>0.4$ ) will be larger the finer the cement PSD [54], as shown in Fig. 7, once again due to interparticle spacing considerations. Silica fume, because of its extremely small particle size along with the high chemical shrinkage accompanying its pozzolanic reaction, can drastically increase the measured RH reduction during early-age hydration [50,55].

## 3. Autogenous shrinkage of cement systems/early-age cracking

Until about the time of set, the chemical shrinkage occurring during cement hydration is accompanied by an equivalent overall volumetric reduction of the “fluid” material [56,57]. During set, the cement paste develops a finite resistance to further volumetric reductions and beyond setting, the measured autogenous deformation is much smaller (up to two orders of magnitude less) than the chemical shrinkage. In the past, autogenous shrinkage has been measured using either a volumetric (latex membrane) or a linear (sealed corrugated tube) method [57–59], but recently, Lura and Jensen have completed a detailed investigation that suggests that the former is an inappropriate method due mainly to the confounding influence of water ingress through the membrane during the measurement time [60]. The linear method for cement pastes and mortars [58]

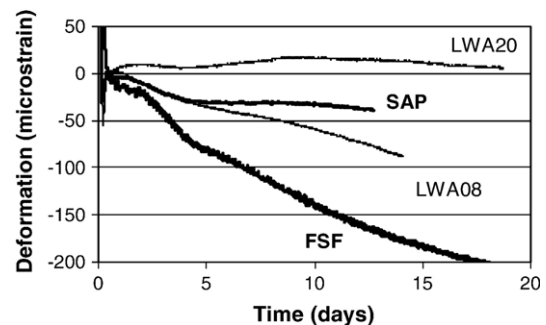


Fig. 9. Measured autogenous deformation vs. time for various mortars ( $w/c=0.3$ ) with and without IC, during sealed hydration at 30 °C; FSF indicates the control mortar prepared with a blended cement containing fine silica fume (8% mass fraction) [74]. SAP refers to the addition of 0.4% superabsorbent polymer particles by mass of cement. LWA08 and LWA20 refer to the LWA replacing 8% and 20% of the normal weight sand by mass, respectively.

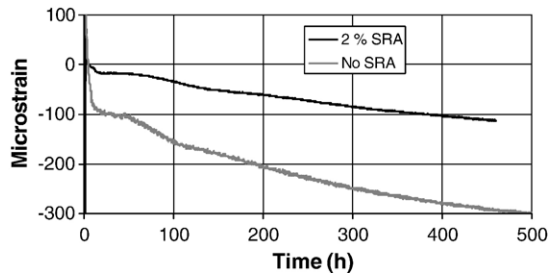


Fig. 10. Differences in autogenous deformation [58] for cement mortars ( $w/c=0.35$ ) with and without SRA, cured under sealed conditions at 30 °C [10].

is currently under consideration for standardization by the ASTM C09.68 Volume Change subcommittee.

The capillary tension ( $\sigma_{\text{cap}}$ ) created in the pore solution during self-desiccation results in the autogenous deformation of the porous material (concrete). In this case, the deformation can be estimated as [61,62]:

$$\varepsilon = \frac{S\sigma_{\text{cap}}}{3} * \left( \frac{1}{K} - \frac{1}{K_s} \right) \quad (2)$$

where  $\varepsilon$  is the linear strain or shrinkage,  $S$  is the saturation (fraction with values between 0 and 1) or fraction of water-filled porosity,  $K$  is the bulk modulus of the porous material (Pa) with empty pores (dry), and  $K_s$  is the bulk modulus of the solid framework within the porous material (Pa). While Eq. (2) is an approximation for a purely elastic material, it has been applied with some success to cement-based materials [63]. Extensions to include a visco-elastic component (creep) have also been made recently [20]. Baroghel-Bouny has pointed out the inherent similarities between autogenous shrinkage due to internal drying and drying shrinkage due to external drying [64].

Because the capillary stresses are a function of the size of the pores being emptied, autogenous deformation is an extremely strong function of  $w/c$  ratio, increasing dramatically as the  $w/c$  is lowered below 0.35 in Portland cement systems. Further dramatic increases are observed in systems containing silica fume and slag additions [59,65–67]. At a constant  $w/c$  and degree of hydration, as shown in Fig. 8, autogenous shrinkage is much greater in systems prepared with a finer cement. In fact, for the two coarser cements in Fig. 8, an early-age autogenous expansion is observed, most likely due to swelling induced by hydration product (such as ettringite) formation [54].

The extension from measuring autogenous shrinkage to predicting early-age cracking is not an easy task. Many of the properties that must be properly accounted for are discussed in a recent paper by Moon et al. [68]. Several of the existing models for predicting field performance with respect to early-age cracking, however, already do include both thermal and autogenous effects in some form [32,34,35].

### 3.1. Mitigation of early-age cracking via internal curing

A careful examination of Eqs. (1) and (2) suggests one possible method for avoiding or minimizing early-age cracking

due to autogenous shrinkage. Since the autogenous stresses are controlled by the size of the pores that are being emptied during self-desiccation, these stresses should be significantly reduced by incorporating a reservoir(s) of water into the concrete, contained in pores larger than the capillary pores in the hydrating cement paste. Hence was born the concept of *internal curing* (IC). This idea was first suggested in the literature by Philleo in 1991 [69]. To date, efforts have been made to utilize saturated lightweight fine aggregates (LWA) [70] (as originally suggested by Philleo), superabsorbent polymers (SAP) [71], and water-saturated wood products [72] as the IC reservoirs. In 2005, the idea moved from being a laboratory concept to being a field reality at several job sites in the U.S., including a large paving project in Texas where 238 000 cubic yards (181 000 cubic meters) of concrete proportioned with IC via saturated LWA were batched and placed over the course of a few months [73]. The author inspected this concrete in December 2005 (likely during its first freeze/thaw cycle); only two cracks were observed, one of which was located where an expansion joint was missing so that the concrete had made just one of its own.

In addition to changing the size of the empty pores being created within the concrete microstructure, the IC water will also contribute to an increased hydration of the surrounding cement paste. The efficiency and effectiveness of IC has thus been assessed by measurements of compressive strength, degree of hydration, internal relative humidity, autogenous shrinkage, and restrained shrinkage and creep [21,71,74,75]. For example, Fig. 9 shows measured autogenous deformations vs. time for a series of high-performance mortars prepared without and with several different IC reservoirs [74]. In each case, the addition of the IC water reservoirs resulted in a substantial reduction in the measured autogenous shrinkage at early ages. The ability of the LWA and SAP additions to significantly reduce autogenous shrinkage is clearly indicated. Recently, four-dimensional (3 spatial and time) X-ray microtomography experiments have been conducted to directly observe water movement from saturated fine LWA to the surrounding cement paste during the first two days of sealed isothermal hydration (30 °C) [76].

The amount of internal curing water needed to maintain saturation of the capillary porosity is directly related to the chemical shrinkage of the cementitious materials in a concrete.

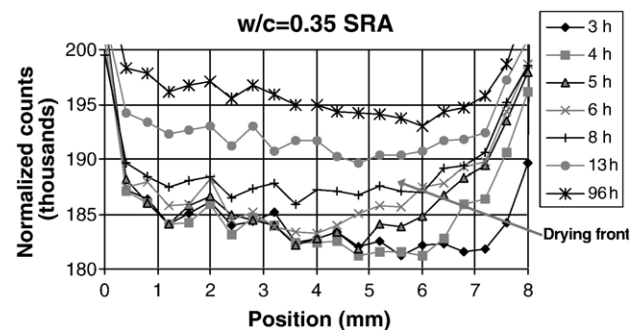


Fig. 11. Normalized counts for X-rays transmitted through a  $w/c=0.35$  Portland cement paste with a 2% SRA addition by mass of cement, immediately exposed to drying conditions (23 °C and 50% RH), as a function of curing time (3 h to 96 h) and depth [10]. Top of specimen is located at about 8 mm.

For LWA reservoirs, this amount can be calculated according to [77]:

$$M_{LWA} = \frac{C_f * CS * \alpha_{max}}{S * \phi_{LWA}} \quad (3)$$

where:  $M_{LWA}$  = mass of (dry) LWA needed per unit volume of concrete ( $\text{kg}/\text{m}^3$  or  $\text{lb}/\text{yd}^3$ ),  $C_f$  = cement factor (content) for concrete mixture ( $\text{kg}/\text{m}^3$  or  $\text{lb}/\text{yd}^3$ ),  $CS$  = chemical shrinkage of cement (grams of water/gram of cement or  $\text{lb}/\text{lb}$ ) at a degree of hydration equal to 100%,  $\alpha_{max}$  = maximum expected degree of hydration of cement,  $S$  = degree of saturation of aggregate (0–1), and  $\phi_{LWA}$  = absorption of lightweight aggregate ( $\text{kg}$  water/ $\text{kg}$  dry LWA or  $\text{lb}/\text{lb}$ ), or more appropriately desorption from saturated surface dry conditions down to about 93% RH. Similar calculations can be employed for SAPs [71] or other sources for the IC water. In addition to supplying the needed volume of curing water, the spatial distribution of the water is also important. In this respect, using fine LWA as opposed to coarse LWA is preferable due to its more homogeneous and closer spaced distribution of the individual IC reservoirs throughout the concrete volume [78,79].

### 3.2. Mitigation of early-age cracking via shrinkage-reducing admixtures

In the previous section, an approach was presented for reducing autogenous shrinkage and early-age cracking by basically increasing the  $r$  term in Eq. (1). Another option is to reduce the magnitude of  $\gamma$ , the surface tension of the pore solution. Such a reduction can be conveniently achieved by the addition of a shrinkage-reducing admixture (SRA) to the mixture. First employed in Japan over twenty years ago [80], SRAs have been utilized to reduce drying shrinkage for the past ten years or so in the U.S. [81,82]. The addition of a few percent SRA (by mass of cement) can reduce the measured surface tension of the concrete pore solution by a factor of two [5,10]. All other properties (contact angle, etc.) remaining equal, this will result in half the capillary tension according to Eq. (1), which should translate into half the autogenous strain according to Eq. (2). This hypothesized reduction in autogenous shrinkage for systems containing SRA has been verified experimentally as exemplified in Fig. 10 [10,83–85].

The addition of an SRA has another significant influence on the early-age properties of a cement-based material. As shown in Fig. 11, according to X-ray transmission measurements, the drying profile generated in the presence of an SRA is vastly different from that generated in a system with no SRA (see Fig. 3 for example) at early ages ( $\leq 8$  h). The SRA results in a drying front that penetrates into the specimen from the surface exposed to the drying environment, while the interior of the specimen remains saturated [10]. Apparently, as pore solution is initially drawn by capillary forces to the surface to evaporate, the remaining solution at the surface will contain a greater concentration of SRA than the solution within the interior of the specimen. Just as water is drawn from a coarser pore system to a finer one in bilayer composites [6] due to the differential in

capillary forces, the surface layer will no longer be able to “pull” water from the higher surface tension water below; confirmatory measurements of these phenomena have been made previously on bilayer (SRA over no SRA and no SRA over SRA) composite specimens [10]. This results in a reduced evaporation rate in a system with an SRA relative to a system with no SRA addition [10,85]. In regards to pore solution movement within a specimen, it is also worth mentioning that the measured viscosity of a typical 10% SRA solution in distilled water is about 50% higher than that of distilled water alone [86], implying a slower internal “flow rate”. As indicated by Lura et al. [5], the addition of the SRA thus results in “less evaporation, reduced settlement, reduced capillary tension, and lower crack-inducing stresses at the topmost layer of the mortar,” consistent with the experimental results of Esping and Löfgren for self-consolidating concretes [85]. These effects all combine to provide a reduction in the propensity to form plastic shrinkage cracks when exposed to a drying environment [5,85]. Recently [87], it has been shown that a similar reduction in evaporative water loss can be achieved by the topical application of an SRA solution (10% or 20% by mass in water) as a curing solution. Timely application of the SRA solution to the top surface of mortars being exposed to a 50% RH environment resulted in significant reductions in subsequent evaporative water loss and significant increases in the degree of hydration achieved in the specimens at longer ages [87].

By simply changing the surface tension (and viscosity) of the pore solution, the early-age properties of cement-based materials can be significantly modified. In addition to the influences on drying rates and internal stress development, SRAs also increase the freezable water content of cement pastes cured under saturated conditions at early ages [1,86], which may have negative implications for the early-age frost resistance of these materials. This paper reinforces the critical role that water menisci play in the performance of partially saturated cement-based materials at early ages and beyond. More research on this topic should result both in improved early-age performance, particularly in terms of avoiding early-age cracking, and in more durable concrete in the longer term.

## References

- [1] D.P. Bentz, Ten observations from experiments to quantify water movement and porosity percolation in hydrating cement pastes, in: B. Mobasher, J. Skalny (Eds.), *Transport Properties and Concrete Quality: Materials Science of Concrete*, American Ceramic Society, Westerville, OH, 2007, pp. 3–18.
- [2] D.P. Bentz, Influence of curing conditions on water loss and hydration in cement pastes with and without fly ash substitution, NISTIR 6886, U.S. Department of Commerce, July 2002.
- [3] D.P. Bentz, K.K. Hansen, Preliminary observations of water movement in cement pastes during curing using X-ray absorption, *Cem. Concr. Res.* 30 (2000) 1157–1168.
- [4] Guide to Curing Concrete (ACI 308.R-01), ACI Manual of Concrete Practice, American Concrete Institute, Farmington Hills, MI, 2001.
- [5] P. Lura, B. Pease, G. Mazzotta, F. Rajabipour, J. Weiss, Influence of shrinkage-reducing admixtures on the development of plastic shrinkage cracks, *ACI Mater. J.* 104 (2) (2007) 187–194.
- [6] D.P. Bentz, K.K. Hansen, H.D. Madsen, F.A. Vallee, E.J. Griesel, Drying/hydration in cement pastes during curing, *Mat. Struct.* 34 (2001) 557–565.



- [7] P. Coussot, Scaling approach of the convective drying of a porous medium, *Eur. Phys. J.*, B 15 (3) (2000) 557–566.
- [8] G.W. Scherer, The theory of drying, *J. Am. Ceram. Soc.* 73 (1) (1990) 3–14.
- [9] P. Coussot, C. Gauthier, D. Nadji, J.C. Borgotti, P. Vie, F. Bertrand, Mouvements capillaires durant le séchage d'une pâte granulaire, *C.R. Acad. Sci. (Paris) t 327 (Série II b)* (1999) 1101–1106.
- [10] D.P. Bentz, M.R. Geiker, K.K. Hansen, Shrinkage-reducing admixtures and early age desiccation in cement pastes and mortars, *Cem. Concr. Res.* 31 (7) (2001) 1075–1085.
- [11] S.P. Jiang, J.C. Mutin, A. Nonat, Studies on mechanism and physico-chemical parameters at the origin of the cement setting. I. The fundamental processes involved during the cement setting, *Cem. Concr. Res.* 25 (4) (1995) 779–789.
- [12] R. D'Angelo, T. Plona, L. Schwartz, P. Coveney, Ultrasonic measurements on hydrating cement slurries: the onset of shear wave propagation, *Adv. Cem.-Based Mater.* 2 (1) (1995) 8–14.
- [13] C.J. Haecker, D.P. Bentz, X.P. Feng, P.E. Stutzman, Prediction of cement physical properties by virtual testing, *Cem. Inter.* 1 (3) (2003) 86–92.
- [14] A. Princigallo, P. Lura, K. van Breugel, G. Levita, Early development of properties in a cement paste: a numerical and experimental study, *Cem. Concr. Res.* 33 (2003) 1013–1020.
- [15] J.W. Bullard, M. D'Ambrosia, Z. Grasley, W. Hansen, N. Kidner, D. Lange, P. Lura, T.O. Mason, J. Moon, F. Rajabipour, G. Sant, S. Shah, T. Voight, S. Wanson, J. Weiss, L. Woo, A comparison of test methods for early-age behavior of cementitious materials, Second Edition of the International Symposium on Advances in Concrete Through Science and Engineering, Quebec, 2006.
- [16] D.P. Bentz, Cement hydration: building bridges and dams at the microstructure level, *Mater. Struct.* 40 (4) (2007) 397–404.
- [17] D.P. Bentz, E.J. Garboczi, C.J. Haecker, O.M. Jensen, Effects of cement particle size distribution on performance properties of cement-based materials, *Cem. Concr. Res.* 29 (1999) 1663–1671.
- [18] Y. Akkaya, T. Voigt, K.V. Subramaniam, S.P. Shah, Nondestructive measurement of concrete strength gain by an ultrasonic wave reflection method, *Mater. Struct.* 36 (262) (2003) 507–514.
- [19] B.F. Dela, Eigenstresses in hardening concrete, Ph.D. Thesis, The Technical University of Denmark, Lyngby, Denmark (2000).
- [20] Z.C. Grasley, D.A. Lange, A.J. Brinks, M.D. D'Ambrosia, Modeling autogenous shrinkage of concrete accounting for creep caused by aggregate restraint, in: B. Persson, D. Bentz, L.-O. Nilsson (Eds.), Proceedings of the 4th International Seminar on Self-Desiccation and Its Importance in Concrete Technology, NIST, Gaithersburg, MD, 2005, pp. 78–94.
- [21] P. Lura, Autogenous deformation and internal curing of concrete, Ph.D. Thesis, Technical University of Delft, Delft, The Netherlands (2003).
- [22] D.P. Bentz, Transient plane source measurements of the thermal properties of hydrating cement pastes, *Mater. Struct.* in press.
- [23] D.P. Bentz, O.M. Jensen, A.M. Coats, F.P. Glasser, Influence of silica fume on diffusivity in cement-based materials. I. Experimental and computer modeling studies on cement pastes, *Cem. Concr. Res.* 30 (2000) 953–962.
- [24] O. Bjontegaard, Thermal dilation and autogenous deformation as driving forces to self-induced stresses in high performance concrete, Ph.D. Thesis, Norwegian University of Science and Technology, Norway (1999).
- [25] K. Brown, A.W. Brown, B.G. Colpitts, T.W. Bremner, The mitigation of measurement inaccuracies of Brillouin scattering based fiber optic sensors through bonded fiber temperature calibrations, 7th Cansmart Workshop: Smart Materials and Structures, Montreal, Quebec, Canada, 2004, pp. 317–324.
- [26] H.F.W. Taylor, *Cement Chemistry*, 2nd edition, Thomas Telford, London, 1997.
- [27] M. Fukuhara, S. Goto, K. Asaga, M. Daimon, R. Kondo, Mechanisms and kinetics of  $C_4AF$  hydration with gypsum, *Cem. Concr. Res.* 11 (1981) 407–414.
- [28] V. Waller, F. De Larrard, P. Roussel, Modelling the temperature rise in massive HPC structures, 4th International Symposium on Utilization of High-Strength/High-Performance Concrete, RILEM S.A.R.L., Paris, 1996, pp. 415–421.
- [29] ASTM C186-05, Standard test method for heat of hydration of hydraulic cement, Volume 04.01, ASTM International, West Conshohocken, PA, 2005.
- [30] L. Wadso, An experimental comparison between isothermal calorimetry, semi-adiabatic calorimetry and solution calorimetry for the study of cement hydration, Final Report NORDTEST project 1534-01, Lund University, Lund, Sweden, 2002.
- [31] D.P. Bentz, Verification, validation, and variability of virtual standards, in: J.J. Beaudoin, J.M. Makar, L. Raki (Eds.), Proceedings of the 12th International Congress on the Chemistry of Cement, 2007.
- [32] P.E. Roelfstra, T.A.M. Salet, J.E. Kuiks, Defining and application of stress-analysis-based temperature difference limits to prevent early-age cracking in concrete structures, Proceedings #25 of the International RILEM Symposium: Thermal Cracking in Concrete at Early Ages, Munich, 1994, pp. 273–280.
- [33] D. Kapila, J. Falkowsky, J.L. Plawsky, Thermal effects during the curing of concrete pavements, *ACI Mater. J.* 94 (2) (1997) 119–128.
- [34] B.F. McCullough, R.O. Rasmussen, Fast-track paving: concrete temperature control and traffic opening criteria for bonded concrete overlays, FHWA-RD-98-167 (1999).
- [35] K. Maekawa, R. Chaube, T. Kishi, Modelling of Concrete Performance: Hydration, Microstructure Formation, and Mass Transport, E&FN Spon, London, 1999.
- [36] D.P. Bentz, A computer model to predict the surface temperature and time-of-wetness of concrete pavements and bridge decks, NISTIR 6551, Department of Commerce, U.S., 2000.
- [37] G.S. Wojcik, The interaction between the atmosphere and curing concrete bridge decks, Ph.D. Thesis, State University of New York, New York (2001).
- [38] T.C. Powers, Adsorption of water by Portland cement paste during the hardening process, *Ind. Eng. Chem.* 27 (1935) 790–794.
- [39] M.R. Geiker, Studies of Portland cement hydration: measurements of chemical shrinkage and a systematic evaluation of hydration curves by means of the dispersion model, Ph.D. Thesis, Technical University of Denmark, Lyngby, Denmark (1983).
- [40] ASTM C1608-05, Test method for chemical shrinkage of hydraulic cement paste, Volume 04.01, ASTM International, West Conshohocken, PA, 2005.
- [41] E. Tazawa (Ed.), *Autogenous Shrinkage of Concrete*, E&FN Spon, London, 1999, pp. 53–55.
- [42] T.C. Powers, L.E. Copeland, H.M. Mann, Capillary continuity or discontinuity in cement paste, *PCA Bull. No. 10* (1959) 2–12.
- [43] D.P. Bentz, E.J. Garboczi, Percolation of phases in a three-dimensional cement paste microstructure model, *Cem. Concr. Res.* 21 (2) (1991) 325–344.
- [44] D.P. Bentz, Three-dimensional computer simulation of Portland cement hydration and microstructure development, *J. Am. Ceram. Soc.* 80 (1) (1997) 3–21.
- [45] H. Justnes, E.J. Sellevold, B. Reyniers, D. Van Loo, A. van Gemert, F. Verboven, D. Van Gemert, The influence of cement characteristics on chemical shrinkage, in: E. Tazawa (Ed.), *Autogenous Shrinkage of Concrete*, E&FN Spon, London, 1999, pp. 71–80.
- [46] P. Mounanga, A. Khelidj, A. Loukili, V. Baroghel-Bouny, Predicting  $Ca(OH)_2$  content and chemical shrinkage of hydrating cement pastes using analytical approach, *Cem. Concr. Res.* 34 (2) (2004) 255–265; Erratum published in, *Cem. Concr. Res.* 35 (2005) 423–424.
- [47] O.M. Jensen, The pozzolanic reaction of silica fume, M.S. Thesis, Technical Report TR229/90, Technical University of Denmark, Lyngby, Denmark, 1990 (in Danish).
- [48] C. Hua, P. Acker, A. Erlacher, Analyses and models of the autogenous shrinkage of hardening cement pastes, *Cem. Concr. Res.* 25 (7) (1995) 1457–1468.
- [49] Self-Desiccation and Its Importance in Concrete Technology, in: B. Persson, G. Fagerlund (Eds.), Proceedings of the 1st International Seminar, Report TVBM-3075, Lund University, Lund, Sweden, 1997.
- [50] O.M. Jensen, P.F. Hansen, Autogenous relative humidity change in silica fume-modified cement paste, *Adv. Cem. Res.* 7 (25) (1995) 33–38.
- [51] Z.C. Grasley, M.D. D'Ambrosia, D.A. Lange, Internal relative humidity and drying stress gradients in concrete, *Mater. Struct.* 39 (9) (2006) 901–909.
- [52] C. Andrade, J. Sarria, C. Alonso, Relative humidity in the interior of concrete exposed to natural and artificial weathering, *Cem. Concr. Res.* 29 (1999) 1249–1259.



- [53] O.M. Jensen, P.F. Hansen, E.E. Lachowski, F.P. Glasser, Clinker mineral hydration at reduced relative humidities, *Cem. Concr. Res.* 29 (9) (1999) 1505–1512.
- [54] D.P. Bentz, O.M. Jensen, K.K. Hansen, J.F. Oleson, H. Stang, C.J. Haecker, Influence of cement particle size distribution on early age autogenous strains and stresses in cement-based materials, *J. Am. Ceram. Soc.* 84 (1) (2001) 129–135.
- [55] P. McGrath, R.D. Hooton, Self-desiccation of Portland cement and silica fume modified mortars, in: S. Mindess (Ed.), *Ceramic Transactions*, Vol. 16, *Advances in Cementitious Materials*, The American Ceramic Society, Inc., Westerville, OH, 1991, pp. 489–500.
- [56] T.A. Hammer, C. Heese, Early age chemical shrinkage and autogenous deformation of cement pastes, in: B. Persson, G. Fagerlund (Eds.), *Proceedings of the 2nd International Seminar on Self-Desiccation and Its Importance in Concrete Technology*, Lund University, Lund, Sweden, 1999, pp. 7–13.
- [57] L. Barcelo, S. Boivin, S. Rigaud, P. Acker, B. Clavaud, C. Boulay, Linear vs. volumetric autogenous shrinkage measurement: material behaviour or experimental artefact? *Ibid.* (1999) 109–125.
- [58] O.M. Jensen, P.F. Hansen, A dilatometer for measuring autogenous deformation in hardening Portland cement paste, *Mater. Struct.* 28 (181) (1995) 406–409.
- [59] O.M. Jensen, P.F. Hansen, Autogenous deformation and change of the relative humidity in silica fume-modified cement paste, *ACI Mater. J.* 93 (6) (1996) 539–543.
- [60] P. Lura, O.M. Jensen, Volumetric measurement in water bath — an inappropriate method to measure autogenous strain of cement paste, PCA R&D Serial No. 2925, Portland Cement Association, Skokie, IL, 2005.
- [61] D.P. Bentz, E.J. Garboczi, D.A. Quenard, Modeling drying shrinkage in reconstructed porous materials: application to porous Vycor glass, *Model Simul. Mater. Sci. Eng.* 6 (3) (1998) 211–236.
- [62] J.K. MacKenzie, The elastic constants of a solid containing spherical holes, *Proc. Phys. Soc.* 683 (1950) 2–11.
- [63] P. Lura, O.M. Jensen, K. van Breugel, Autogenous shrinkage in high-performance cement paste: an evaluation of basic mechanisms, *Cem. Concr. Res.* 33 (2) (2003) 223–232.
- [64] V. Baroghel-Bouny, Experimental investigation of self-desiccation in high-performance materials — comparison with drying behaviour, in reference 49, 1997, pp. 72–87.
- [65] K.M. Lee, H.K. Lee, S.H. Lee, G.Y. Kim, Autogenous shrinkage of concrete containing granulated blast-furnace slag, *Cem. Concr. Res.* 36 (7) (2006) 1279–1285.
- [66] D.P. Bentz, Internal curing of high-performance blended cement mortars, *ACI Mater. J.* 104 (4) (2007) 408–414.
- [67] S. Hanehara, H. Hirao, H. Uchikawa, Relationships between autogenous shrinkage and the microstructure and humidity changes at inner part of hardened cement paste at early age, in: E. Tazawa (Ed.), *Autogenous Shrinkage of Concrete*, E&FN Spon, London, 1999, pp. 93–104.
- [68] J.H. Moon, F. Rajabipour, B. Pease, J. Weiss, Autogenous shrinkage, residual stress, and cracking in cementitious composites: The influence of internal and external restraint, in: B. Persson, D. Bentz, L.-O. Nilsson (Eds.), *Proceedings of the 4th International Seminar on Self-Desiccation and Its Importance in Concrete Technology*, NIST, Gaithersburg, MD, 2005, pp. 1–20.
- [69] R.E. Philleo, Concrete science and reality, in: J. Skalny, S. Mindess (Eds.), *Materials Science of Concrete II*, American Ceramic Society, Westerville, OH, 1991, pp. 1–8.
- [70] S. Weber, H.W. Reinhardt, A blend of aggregates to support curing of concrete, in: I. Holand, T.A. Hammer, P. Fluge (Eds.), *Proceedings of the International Symposium on Structural Lightweight Aggregate Concrete*, Sandefjord, Norway, 1995, pp. 662–671.
- [71] O.M. Jensen, P.F. Hansen, Water-entrained cement-based materials: II. Experimental observations, *Cem. Concr. Res.* 32 (6) (2002) 973–978.
- [72] B. Mohr, L. Premenko, H. Nanko, K.E. Kurtis, Examination of wood-derived powders and fibers for internal curing of cement-based materials, in: B. Persson, D. Bentz, L.-O. Nilsson (Eds.), *Proceedings of the 4th International Seminar on Self-Desiccation and Its Importance in Concrete Technology*, NIST, Gaithersburg, MD, 2005, pp. 229–244.
- [73] V. Villarreal, D. Crocker, Building better pavements through internal hydration, *Concr. Inter* 29 (2) (2007) 32–36.
- [74] M.R. Geiker, D.P. Bentz, O.M. Jensen, Mitigating autogenous shrinkage by internal curing, in: J.P. Ries, T.A. Holm (Eds.), *ACI SP-218, High Performance Structural Lightweight Concrete*, American Concrete Institute, Farmington Hills, MI, 2004, pp. 143–154.
- [75] D. Cusson, D.T. Hooegeveen, Internally-cured high-performance concrete under restrained shrinkage and creep, in *CONCREEP 7 Workshop on Creep, Shrinkage, and Durability of Concrete and Concrete Structures*, Nantes, France, 2005, pp. 579–584.
- [76] D.P. Bentz, P.M. Halleck, A.S. Grader, J.W. Roberts, Direct observation of water movement during internal curing using X-ray microtomography, *Concr. Inter.* 28 (10) (2006) 39–45.
- [77] D.P. Bentz, P. Lura, J.W. Roberts, Mixture proportioning for internal curing, *Concr. Inter.* 27 (2) (2005) 35–40.
- [78] D.P. Bentz, K.A. Snyder, Protected paste volume in concrete: Extension to internal curing using saturated lightweight fine aggregates, *Cem. Concr. Res.* 29 (1999) 1863–1867.
- [79] K. van Breugel, P. Lura, Effect of initial moisture content and particle size distribution of lightweight aggregates on autogenous deformation, in: S. Helland, I. Holand, S. Smeplass (Eds.), *Proceedings of the 2nd International Symposium on Structural Lightweight Concrete*, Kristiansand, Norway, 2000, pp. 453–462.
- [80] T. Sato, T. Goto, K. Sakai, Mechanism for reducing drying shrinkage of hardened cement by organic additives, *CAJ Rev.* (1983) 52–54.
- [81] K.J. Folliard, N.S. Berke, Properties of high-performance concrete containing shrinkage-reducing admixtures, *Cem. Concr. Res.* 27 (9) (1997) 1357–1364.
- [82] C.K. Nmai, R. Tomita, F. Hondo, J. Buffenberger, Shrinkage-reducing admixtures, *Concr. Inter.* 20 (4) (1998) 31–37.
- [83] B. Rongbing, S. Jian, Synthesis and evaluation of shrinkage-reducing admixtures for cementitious materials, *Cem. Concr. Res.* 35 (3) (2005) 445–448.
- [84] D.P. Bentz, M.R. Geiker, O.M. Jensen, On the mitigation of early age cracking, in: B. Persson, G. Fagerlund (Eds.), *Proceedings of the 3rd International Seminar on Self-Desiccation and Its Importance in Concrete Technology*, Lund, Sweden, 2002, pp. 195–203.
- [85] O. Esping, I. Löfgren, Investigation of early age deformation in self-consolidating concrete, *Proceedings of the 2nd International RILEM Symposium “Advances in Concrete through Science and Engineering”*, 2006.
- [86] D.P. Bentz, Influence of shrinkage-reducing admixtures on drying, autogenous shrinkage, and freezable water content of cement pastes at early ages, *J. Adv. Concr. Tech.* 4 (3) (2006) 423–429.
- [87] D.P. Bentz, Curing with shrinkage-reducing admixtures: beyond drying shrinkage reduction, *Concr. Inter.* 27 (10) (2005) 55–60.