EARLY-AGE CRACKING REVIEW: MECHANISMS, MATERIAL PROPERTIES, AND MITIGATION STRATEGIES

Cementitious Barriers Partnership

November 2009

CBP-TR-2009-002-C3, Rev. 0

ACKNOWLEDGEMENTS

Disclaimer

Printed in the United States of America

United State Department of Energy
Office of Environmental Management
Washington, DC

This document is available on the CBP website: http://cementbarriers.org/
and
Savannah River National Laboratory website: http://srnl.doe.gov

FOREWORD

The Cementitious Barriers Partnership (CBP) Project is a multi-disciplinary, multi-institutional collaboration supported by the United States Department of Energy (US DOE) Office of Waste Processing. The objective of the CBP project is to develop a set of tools to improve understanding and prediction of the long-term structural, hydraulic, and chemical performance of cementitious barriers used in nuclear applications.

A multi-disciplinary partnership of federal, academic, private sector, and international expertise has been formed to accomplish the project objective. In addition to the US DOE, the CBP partners are the United States Nuclear Regulatory Commission (NRC), the National Institute of Standards and Technology (NIST), the Savannah River National Laboratory (SRNL), Vanderbilt University (VU) / Consortium for Risk Evaluation with Stakeholder Participation (CRESP), Energy Research Center of the Netherlands (ECN), and SIMCO Technologies, Inc.

The periods of cementitious performance being evaluated are >100 years for operating facilities and > 1000 years for waste management. The set of simulation tools and data developed under this project will be used to evaluate and predict the behavior of cementitious barriers used in near-surface engineered waste disposal systems, e.g., waste forms, containment structures, entombments, and environmental remediation, including decontamination and decommissioning (D&D) activities. The simulation tools also will support analysis of structural concrete components of nuclear facilities (spent-fuel pools, dry spent-fuel storage units, and recycling facilities such as fuel fabrication, separations processes). Simulation parameters will be obtained from prior literature and will be experimentally measured under this project, as necessary, to demonstrate application of the simulation tools for three prototype applications (waste form in concrete vault, high-level waste tank grouting, and spent-fuel pool). Test methods and data needs to support use of the simulation tools for future applications will be defined.

The CBP project is a five-year effort focused on reducing the uncertainties of current methodologies for assessing cementitious barrier performance and increasing the consistency and transparency of the assessment process. The results of this project will enable improved risk-informed, performance-based decision-making and support several of the strategic initiatives in the DOE Office of Environmental Management Engineering & Technology Roadmap. Those strategic initiatives include 1) enhanced tank closure processes; 2) enhanced stabilization technologies; 3) advanced predictive capabilities; 4) enhanced remediation methods; 5) adapted technologies for site-specific and complex-wide D&D applications; 6) improved SNF storage, stabilization and disposal preparation; 7) enhanced storage, monitoring and stabilization systems; and 8) enhanced long-term performance evaluation and monitoring.

Christine A. Langton, PhD.
Savannah River National Laboratory

David S. Kosson, PhD.
Vanderbilt University/CRESP

EARLY-AGE CRACKING REVIEW: MECHANISMS, MATERIAL PROPERTIES, AND MITIGATION STRATEGIES

D. P. Bentz
E-mail: dale.bentz@nist.gov
National Institute of Standards and Technology
Gaithersburg, MD 20899

CONTENTS   Page No.

LIST OF TABLES   **Page No.**

LIST OF FIGURES

LIST OF ABBREVIATIONS AND ACRONYMS

ACI	American Concrete Institute
AFm	aluminum ferrite monosulfate hydrate phases
AFt	aluminum ferrite trisulfate hydrate phases
ASTM	American Society for Testing and Materials
$C_p^{crseagg}$	heat capacity of coarse aggregate
$C_p^{fineagg}$	heat capacity of fine aggregate
$c_p^{concrete}$	heat capacity of concrete
c_p^{paste}	heat capacity of cement paste
C_f	cement factor
CBP	Cementitious Barriers Partnership
CS	chemical shrinkage
C_nS	calcium silicate
CTE	coefficient of thermal expansion
d	days (curing time)
E	bulk modulus of porous material
E_s	bulk modulus of solid framework within a porous material
FA	fly ash
H-S	Hashin – Shtrikman (bounds)
HCSS	hard core / soft shell
HPC	high performance concrete
IC	internal curing
k	thermal conductivity
LWA	lightweight aggregate
$M_f j$	mass fraction of jth phase in concrete
$M_f^{fineagg}$	mass fraction of fine aggregate
$M_f^{crseagg}$	mass fraction of coarse aggregate
M_{LWA}	mass of (dry) LWA
PSD	particle size distribution
r	radius of meniscus
R	universal gas constant [8.314 J/(mol·K)]
RH	relative humidity
S	degree of saturation
SF	silica fume
SRA	shrinkage reducing admixture
T	temperature
V_m	molar volume of pore solution
w/c	water to cement ratio
w/cm	water to cementitious material ratio (includes cement + slag cement + fly ash + silica fume

LIST OF ABBREVIATIONS AND ACRONYMS (contd)

x	volume fraction
α_{max}	maximum achievable degree of hydration
ε	linear strain
γ	surface tension
ϕ_{LWA}	absorption (desorption) of lightweight aggregate
σ_{cap}	capillary tension (pressure)
θ	contact angle

EARLY-AGE CRACKING REVIEW: MECHANISMS, MATERIAL PROPERTIES, AND MITIGATION STRATEGIES

D. P. Bentz

National Institute of Standards and Technology

Gaithersburg, MD 20899

ABSTRACT

The goal of long lasting concrete for critical infrastructure applications can only be achieved when early-age cracking is avoided. This includes nuclear facilities, including waste processing, containment and storage facilities and power plant facilities. Consequently, this topic is crucial to the mission of the Cementitious Barriers Partnership (CBP). Since most concrete is cast in place, field conditions, including environmental and workmanship parameters, can significantly influence early-age cracking tendencies. Beyond this, two inherent contributions to early-age cracking are thermal and autogenous deformations. In this chapter, these latter two contributions are reviewed from the three perspectives of basic mechanisms, relevant material properties, and successful mitigation strategies for portland cement-based concrete. Cementitious waste forms have unique chemistry and will need to be considered on a case by case basis.

For thermal deformations, key considerations are hydration rates and the thermophysical properties of the cement paste or concrete. The heat of hydration of the binder sets the limit on the ultimate possible temperature rise of the concrete. Equally important to this ultimate heat of hydration is the hydration rate that governs when and how fast this heat is produced within a cement paste or concrete element. Thermophysical properties of relevance include heat capacity, thermal conductivity, and coefficient of thermal expansion. Methods for measuring these properties are discussed and representative data presented.

Autogenous deformations are driven by the volumetric chemical shrinkage that accompanies the reactions of cementitious binders. Under non-saturated conditions, this chemical shrinkage leads to self-desiccation and the creation of internal stresses and strains. Autogenous shrinkage is generally increased in lower water-to-cementitious materials ratio *(w/cm)* systems and in systems that contain fine supplementary cementitious materials such as silica fume and slag. Measurement of internal relative humidity provides a convenient method for onsite monitoring of the self-desiccation process.

A wide variety of mitigation strategies have been successfully employed to mitigate thermal and autogenous contributions to early-age cracking. Modifications to the mixture proportions such as an increase in *w/cm* ratio, the utilization of a coarser cement, or a partial replacement of cement with a coarse limestone powder can effectively reduce both the maximum temperature rise and the autogenous shrinkage experienced by a concrete mixture. Two other well-developed mitigation strategies, specifically for reducing autogenous shrinkage, are the utilization of shrinkage-reducing admixtures and the application of internal curing, using

pre-wetted lightweight aggregates for example. Both of these have progressed from laboratory evaluation to field applications in recent years and their ability to reduce plastic shrinkage cracking (as well as early-age cracking after set) has been recently documented.

1.0 INTRODUCTION

For the long term performance of concrete to be acceptable and predictable, in general, early-age cracking should be avoided. For example, it is known that the early-age transverse cracking of over 100,000 bridge decks in the U.S. has led to "premature corrosion of the reinforcing steel and spalling of the protective concrete cover, resulting in increased maintenance costs and reduced service life" (Cusson 2005). Improper design practices can contribute to early-age cracking, but for this review, it will be assumed that a correct design has been performed. Additionally, many field practices including concrete placement, finishing, and curing can contribute to early-age cracking, but it will be assumed that these steps are performed in a proper and controlled manner. It is further recognized that field environmental and restraint conditions may be quite different from those employed in conventional laboratory testing. Temperature, relative humidity, and wind extremes may cover a much larger range for a new concrete construction than that investigated in a typical laboratory study where environmental conditions are often held constant. Structural restraint will be a function of design and field conditions and may differ significantly from restraint conditions (if any) employed in lab testing.

The focus of this chapter will thus be on the inherent properties of hardening portland cement-based paste and concrete that contribute to the occurrence of early-age cracking, and mixture proportioning and other mitigation strategies that can be employed to reduce the probability of such cracking. Many of these issues are addressed in further detail in the recent state-of-the-art report produced by the American Concrete Institute (ACI) Committee 231 – Properties of Concrete at Early Ages (ACI 231 2009). While the definition of "early age" is arbitrary and somewhat controversial even within ACI, for the purposes of this chapter, it shall be considered as the time from concrete placement until an age of 7 days (d) (under ordinary field curing temperatures). It should also be recognized that even when cracking does not occur during these first 7 d, the thermal and autogenous stresses that are developed during this time can contribute to later age cracking that may be due to drying or other crack-inducing (degradation) mechanisms. Cementitious waste forms have unique chemistry and will need to be considered on a case by case basis.

Assuming proper design, placement, finishing, and curing, the two major remaining contributions to early-age cracking are the stresses that develop due to thermal and autogenous deformations. The cement hydration and pozzolanic reactions are exothermic, generating significant heat that must be dissipated from the concrete to the surroundings. Two important characteristics for a given concrete mixture in a given structure are the maximum internal temperature achieved and the maximum temperature gradient that exists across the concrete member during curing. When the former is too high (> 60ºC), certain cement hydration phases such as ettringite may become unstable and dissolve; their subsequent and expansive reprecipitation that may occur when the concrete returns to lower temperatures can cause internal and external cracking. In terms of the temperature gradient across the concrete member, if it becomes too large, the induced thermal stresses may exceed the strength of the concrete and cause cracking. Because of this risk of thermal cracking, many specifications detail the maximum allowed values for these two

quantities, particularly in mass concrete structures. Thermal issues are generally more pronounced in larger structures due to their lower surface to volume ratio that reduces the quantity of heat lost to the environment relative to that being generated internally by the hydration reactions. The problem is compounded by the fact that any internal temperature increases also increase the cement hydration rates producing an autoacceleratory thermal response that may be detrimental to short and long term performance.

A second inherent characteristic of the cement hydration and pozzolanic reactions is that they are accompanied by a chemical shrinkage, due to the fact that the reaction products occupy considerably less volume than the reactants. The ultimate chemical shrinkage of a typical hydrating portland cement paste can be on the order of 10% by volume (Bentz 2008). If additional curing water is not readily available, after set, this chemical shrinkage will be accompanied by the creation of empty capillary porosity within the hydrating cement paste, known as self-desiccation. The menisci in remaining partially-filled pores will in turn create autogenous stresses that will produce an autogenous shrinkage that may

lead to early-age cracking when the concrete is restrained (externally or internally). Cracks may be produced in the vicinity of the internal restraints (steel reinforcement and aggregates) or through the depth of the concrete member when sufficient external restraint is present. Unlike thermal cracking, under isothermal conditions, autogenous deformation is inherently size independent. In real world (semi-adiabatic) conditions, however, specimen size will influence autogenous and total shrinkage response (Durán-Herrera et al. 2008).

2.0 THERMAL CRACKING CONSIDERATIONS

2.1 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 and/or thermal cracking 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 (Taylor 1997; Fukuhara et

Table 1. Enthalpies of Complete Hydration for Major Phases of Portland Cement (Taylor 1997; Fukuhara et al. 1981)

Phase[1]	Enthalpy (kJ/kg phase)
C_3S	-517 ±13
C_2S	-262
C_3A	-908, -1672, -1144[+]
C_4AF	-418, -725[+]

+For C_3A and C_4AF hydration, values are for conversion to C_3AH_6, ettringite, and monosulfate (AFm) phase (only for C_3A), respectively. Cement chemistry notation is used throughout this chapter.

---

[1]Cement chemistry notation for oxides related to portland cement: $CaO = C$, $SiO_2 = S$, $Al_2O_3 = A$, $Fe_2O_3 = F$, $SO_3 = \bar{S}$, $CO_2 = \bar{C}$, $K_2O = K$, $Na_2O = N$, $MgO = M$, $H_2O = H$.

al.1981). 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 $Ca(OH)_2$) of about 780 kJ/kg silica fume (Waller, De Larrard & Roussel 1996), while the reactions of fly ash and to a lesser extent slag typically produce less heat than those of portland cement. The latter effect is often compounded by the fact that slag and fly ash are typically much less reactive at early ages than is silica fume. Examples of enthalpy values for hydraulic blast furnace slag include 344 kJ/kg slag and 440 kJ/kg slag (Bensted, 1981) and 461 kJ/kg slag (Kishi and Maekawa, 1995). Generally, the very minor contribution to the total heat of hydration due to the incorporation of limestone filler can be neglected, although its effects on reaction kinetics and the rate of heat release may be significant and should be appropriately taken into consideration (Poppe and De Schutter, 2006).

Heat of hydration is typically measured using a standardized heat of solution technique (ASTM C186-05 2005) or semi-adiabatic methods; a new standard method based on isothermal calorimetry has been developed in the Nordic countries (Wadso 2002) and is now being balloted within the American Society for Testing and Materials (ASTM) C01 Cement Committee (Subcommittee C01.26). Both isothermal and semi-adiabatic calorimeters for cement pastes, mortars, and concretes are readily available from a variety of commercial vendors.

2.2 Thermophysical Property Development – Heat Capacity, Thermal Conductivity, and Coefficient of Thermal Expansion

The dissipation of the heat produced by the hydration reactions will depend strongly on the thermophysical properties of the concrete including density, heat capacity, and thermal conductivity. 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 these thermophysical properties could vary with hydration. As shown in Figure 1, the heat capacity of cement paste is a strong function of both water-to-cement ratio (w/c) and curing conditions (Bentz 2007a). This is mainly due to the high heat capacity of free water (4.18 J/(g•K) vs. about 0.75 J/(g•K) for dry cement powder) that dominates the cement paste heat capacity, so that the cement paste heat capacity decreases as free 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.

In going from cement paste to concrete, a simple law of mixtures can be applied where the heat capacity of the concrete is the mass-weighted average of its components: cement paste, aggregates, steel, and fibers. For a basic unreinforced concrete, the law of mixtures would be (Waller, De Larrard & Roussel 1996):

$$C_p^{concrete} = C_p^{paste} M_f^{paste} + C_p^{fineagg} M_f^{fineagg} + C_p^{crseagg} M_f^{crseagg} \tag{1}$$

where:

c_p^{paste} represents the heat capacity of the hydrating cement paste at the age (degree of hydration) of interest, as provided in Figure 1, and M_f^j is the mass fraction of the jth phase.
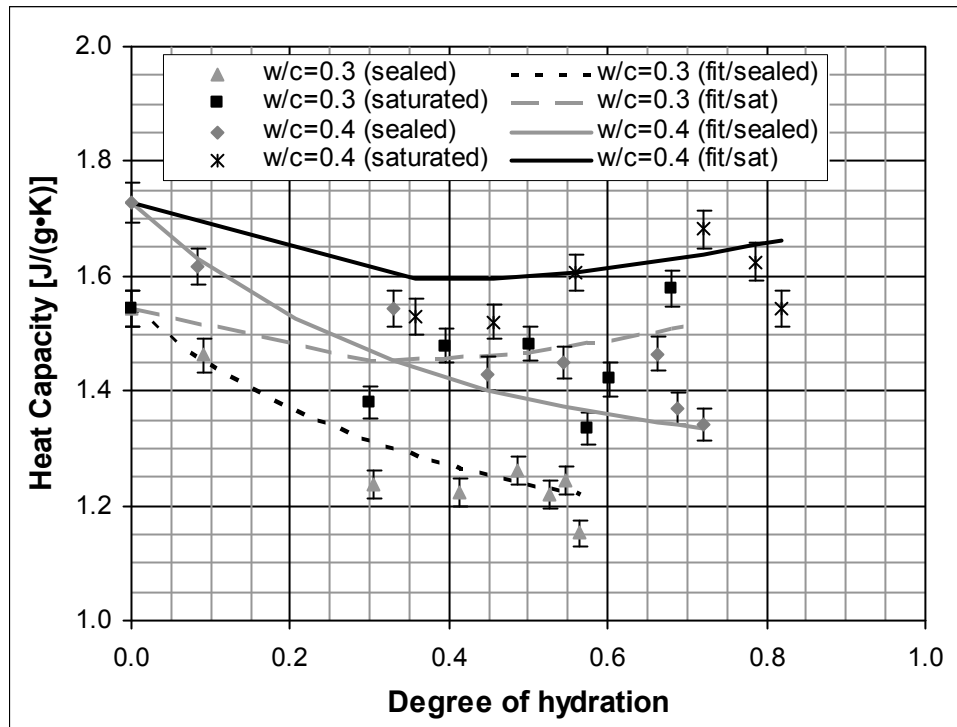
Figure 1. **Measured and Fitted Heat Capacities of Hydrating Cement Paste as A Function of Degree of Hydration, With** *w/c*= **0.3 and** *w/c*= **0.4, Cured Under Saturated or Sealed Conditions at 20°C (Bentz 2007a). Error Bars Indicate A Reproducibility of ± 2% in the Experimental Measurements.**

As shown in Figure 2, 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 in (Bentz 2007a). 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 ± 10%).

For thermal conductivity, in going from cement paste to concrete, the Hashin-Shtrikman (H-S) bounds (Hashin & Shtrikman 1962) can be applied by considering the concrete to be a two-phase composite consisting of aggregates in hydrated cement paste and ignoring any air entrainment. The interfacial transition zones are also ignored, since Figure 2 showed that the thermal conductivity was insensitive to water to cement ratio (*w/c*). Knowing the thermal conductivity of the specific aggregates (Horai 1971) and assuming a value of 1.0 W/(m•K) for the hydrated cement paste, equations (2) and (3) below can be applied to determine lower and upper bounds (k_l and k_h, respectively) for the thermal conductivity of any concrete composite of known mixture proportions. Typically cement paste is considered as phase 1 and the aggregates as phase 2 because the thermal conductivity of most aggregates is higher than the nominal value for cement paste of 1.0 W/(m•K) and because equations (2) and (3) require $k_2 \geq k_1$. Lightweight aggregates with their much lower thermal conductivity could be an exception to this;
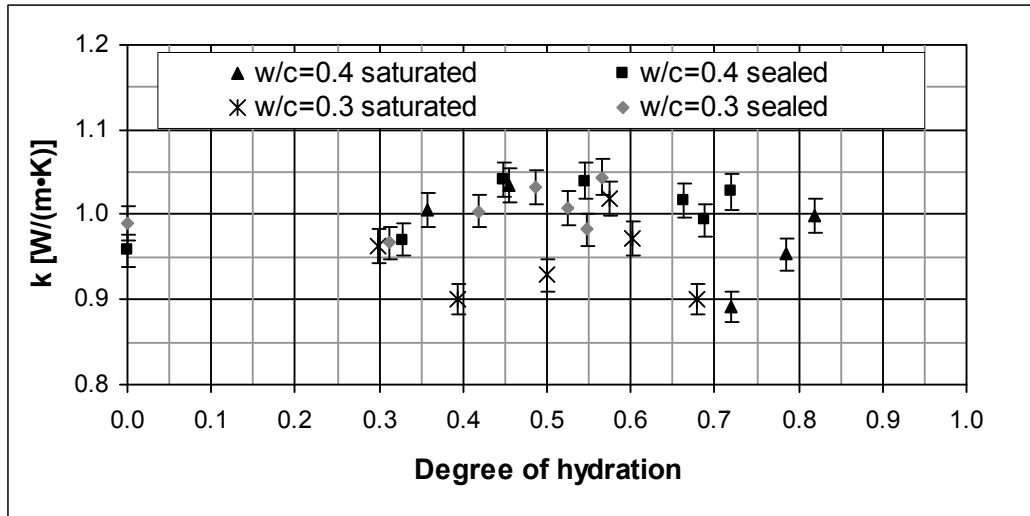
Figure 2. Measured Thermal Conductivity of Hydrating Cement Paste as A Function of Degree of Hydration, with *w/c* **= 0.3 and** *w/c* **= 0.4, Cured Under Saturated or Sealed Conditions at 20°C (Bentz 2007a). Error Bars Indicate A Reproducibility of ± 2% in the Experimental Measurements.**

in that case, the aggregates could be considered as phase 1 and the higher thermal conductivity cement paste as phase 2.) Finally, a reasonable estimate of the thermal conductivity of the concrete of interest could be taken as the mean of these upper and lower bounds.

$$k_l = k_1 + \frac{x_2}{\dfrac{1}{k_2 - k_1} + \dfrac{x_1}{3k_1}} \qquad (2)$$

$$k_h = k_2 + \frac{x_1}{\dfrac{1}{k_1 - k_2} + \dfrac{x_2}{3k_2}} \qquad (3)$$

where:

k_1 and k_2 are the thermal conductivities of the cement paste and aggregate, respectively, and x_1 and x_2 are their respective volume fractions $(x_1 + x_2 = 1)$.

As an example, Figure 3 shows the computed Hashin-Shtrikman bounds for a concrete containing limestone aggregates with $k_2 \approx 3$ W/(m•K) (Kim et al. 2003; Vosteen & Schellschmidt 2003). For the typical cement paste volume fraction of 30% to 35%, the concrete would be expected to have a thermal conductivity of 2.1 W/(m•K) to 2.2 W/(m•K). While the H-S bounds are fairly tight in Figure 3, for siliceous aggregates, such as quartz, with their higher thermal conductivity of ≈ 5 W/(m•K) to 8 W/(m•K) (Horai 1971; Kim et al. 2003; Bougerra et al. 1997), the H-S bounds will be wider and the inaccuracy of using the mean H-S value as an estimate for the concrete could increase.

Equally important to predicting early age thermal cracking is an accurate characterization of the concrete's coefficient of thermal expansion (CTE). This property is particularly difficult to measure at early ages due to the confounding influences of the ongoing hydration and other effects (Bjontegaard 1999). Fiber optic-based techniques may offer an
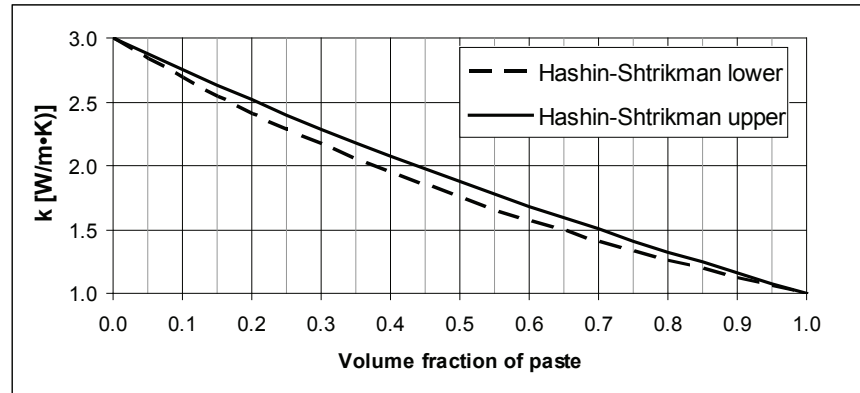
Figure 3. Estimates Based On the H-S Bounds for the Thermal Conductivity of a Concrete as A Function of the Volume Fraction of Paste, Assuming that the Cement Paste Has $k_1 = 1$. W/(m·K) and the Limestone Aggregate Has $k_2 = 3$ W/(m·K) (Bentz 2007a).

in-situ non-destructive solution to this dilemma (Brown et al. 2004; Viviani, Glisic & Smith 2007). CTE values of 10×10^{-6} [K^{-1}] to 12×10^{-6} [K^{-1}] are typically employed for concrete at early ages. Measurement details can be found in the recent ACI state-of-the-art report (ACI 231 2009).

2.3 Modeling Heat of Hydration and Exothermic Hydration Processes

Computer models have been successfully applied for predicting the heat release and temperature rise of cement paste and concrete mixtures (Bentz, Waller & De Larrard 1998; Maekawa, Chaube & Kishi 1999; Bentz 2007c). For example, in the latter case, chemical shrinkage measurements performed to an age of 12 hours on cement pastes were employed to calibrate the kinetics (hydration rate) of a computer model for cement hydration, which was then employed to predict successfully the previously measured 7-day and 28-day heat of hydration results for a number of portland cements. Other computer models go a step further to not only predict heat release and temperature rise but to consider also the generated thermal stresses and propensity for early-age cracking (ACI 231 2009). Examples of these that can be freely downloaded by the general public

include HIPERPAV (http://www.hiperpav.com/) and Concreteworks (http://www.texasconcreteworks.com/).

3.0 AUTOGENOUS SHRINKAGE CONSIDERATIONS

3.1 Chemical Shrinkage

As cement hydrates, the volume of the hydration products is less than that of the starting materials (including water). Powers was the first to quantify the chemical shrinkage (water imbibition) of the various cement clinker phases (Powers 1935). An experimental technique for quantifying chemical shrinkage that was studied in detail by Geiker (Geiker 1983) has been approved by ASTM Committee C01 as Standard Test Method C1608 (ASTM C1608-06 2006). 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 (Tazawa 1999). Due to the depercolation of the capillary porosity that may occur during hydration which limits this water

transport (Powers, Copeland & Mann 1959; Bentz & Garboczi 1991), both the specimen thickness and the w/c must be within a limited range (nominally a few millimeters to 0.4 mm, 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 (Bentz 1997; Justnes et al. 1999; Mounanga et al. 2005), 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 water /g C_nS (C_nS indicating C_2S or C_3S)[1]. 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 (Jensen 1990). Slag and fly ash also generally have chemical shrinkage coefficients that are two to three times those of portland cement (Bentz 2007b). As mentioned earlier, the ultimate chemical shrinkage of a typical hydrating portland cement paste can be on the order of 10% by volume or about 7% by mass. This means that for each 100 g of cement that are reacting, 7 g of additional curing water must be supplied if saturated conditions are to be maintained within the paste microstructure, thus avoiding self-desiccation and possible autogenous shrinkage, stresses, and cracking.

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 (Bentz

1997; Hua, Acker & Erlacher 1995). As shown in the Kelvin-Laplace equation (4) below, the menisci formed in these (partially) empty pores will create a capillary tension within the pore solution and also reduce the internal relative humidity (RH) of the specimen.

$$\sigma_{cap} = \frac{2\gamma\cos\theta}{r} = \frac{-\ln(RH)RT}{V_m} \tag{4}$$

where:

σ_{cap} is the capillary tension (Pa),
γ is the surface tension of the pore solution (N/m),
θ is the contact angle between the pore solution and the capillary pore walls,
V_m is the pore solution molar volume (m3/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 J/(mol•K)], and
T is the absolute temperature in K.

When mitigation strategies are considered later, it will be shown that equation (4) provides valuable insights into two common mitigation strategies, namely surface tension reduction via shrinkage-reducing admixtures (SRAs) and an increase in the size of the pores being emptied via internal curing (IC).

This self-desiccation process is 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 (ed. Persson & Fagerlund 1997).

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 (Jensen and Hansen 1995a) and more recently for field use (Grasley, Ambrosia & Lange 2006), but only a few data from actual field exposures (other than industrial floors) have been published to date (Andrade, Sarria & Alonso 1999). A variety of RH probes that can be readily embedded in the hardening concrete are now commercially available. The reduction in internal RH will also reduce the hydration rates of the remaining cement clinker phases (Bentz 1997; Jensen et al. 1999). According to equation (4), this internal RH reduction will be significantly less in systems with higher *w/c* due to the initially larger spacing between cement particles (larger pore radii) (Bentz and Aitcin 2008). 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 particle size distribution (PSD) (Bentz et al. 2001), as shown in Figure 4. This is once again due to interparticle spacing considerations, since this sets the scale of the initial capillary porosity. 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 (Jensen & Hansen 1995a; McGrath & Hooton 1991).

3.4   Autogenous Shrinkage

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 (Hammer & Heese 1999; Barcelo et al. 1999). During set, the cement paste develops
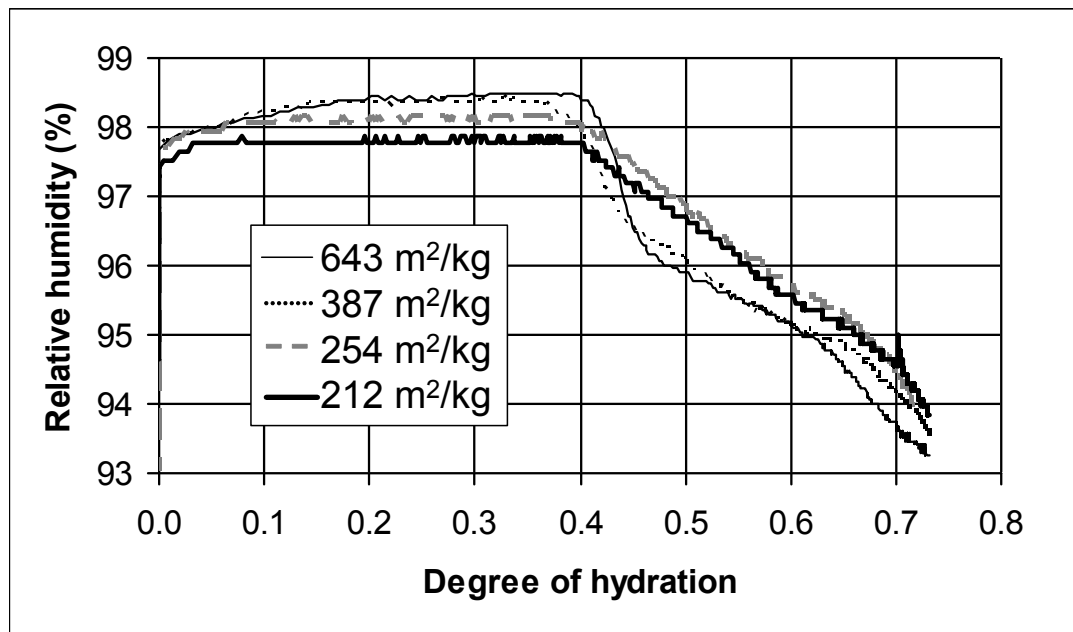

Figure 4. Internal Relative Humidity vs. Degree of Hydration as A Function of Cement Fineness for Cement Pastes Prepared With *w/c* = 0.35 and Cured Under Sealed Conditions at 30ºC (Bentz al.2001).

a finite resistance to further volumetric reductions. After 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 (immersion of a latex membrane) or a linear (sealed corrugated tube) method (Barcelo et al. 1999; Jensen & Hansen 1995b; Jensen & Hansen 1996), 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 (Lura & Jensen 2005). The linear method for cement pastes and mortars (Jensen & Hansen 1995b) is currently being balloted for standardization by the ASTM C09 Concrete and Concrete Aggregates committee.

The capillary tension (σcap in equation (4)) created in the pore solution during self-desiccation results in the autogenous deformation of the porous cementitious materials (e.g., concretes, grouts, and wasteforms). For such materials, the deformation can be estimated as (Bentz, Garboczi & Quenard 1998; MacKenzie 1950):

$$\varepsilon = \frac{S\sigma_{cap}}{3}\left(\frac{1}{E} - \frac{1}{E_s}\right) \qquad (5)$$

where:

ε is the linear strain or shrinkage,
S is the saturation (fraction with values between 0 and 1) or fraction of water-filled porosity,
E is the bulk modulus of the porous material (Pa) with empty pores (dry), and
E_s is the bulk modulus of the solid framework within the porous material (Pa).

While equation (5) is an approximation for a purely elastic material, it has been applied with some success to cement-based materials (Lura, Jensen & van

Breugel 2003). Extensions to include a visco-elastic component (creep) have also been made (Grasley et al. 2005). Baroghel-Bouny has pointed out the inherent similarities between autogenous shrinkage due to internal drying and drying shrinkage due to external drying (Baroghel-Bouny 1997).

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 (Bentz 2007b; Jensen & Hansen 1996; Lee et al. 2006). Conversely, due to its generally low reactivity at early ages, fly ash additions often function similar to an inert filler and may decrease autogenous deformation due to an increase in the effective w/c of the mixture (Bentz 2007b). At a constant w/c and degree of hydration, as shown in Figure 5, autogenous shrinkage is much greater in systems prepared with a finer cement. In fact, for the two coarser cements in Figure 5, an early age autogenous expansion is observed, most likely due to swelling induced by hydration product (such as ettringite or calcium hydroxide) formation (Bentz et al. 2001).

3.5 Modeling Autogenous Shrinkage and Early-Age Cracking

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 (Moon et al. 2005). 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 (Roelfstra, Salet & Kuiks 1994; McCullough & Rasmussen 1999; Ruiz et al. 2005; Maekawa, Chaube & Kishi 1999; Tazawa 1999). Internal damage caused by self-desiccation
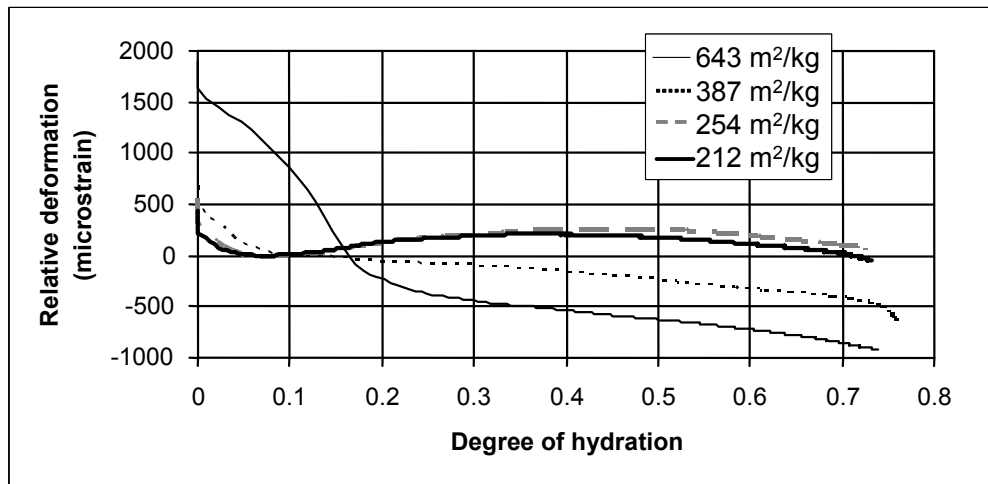
Figure 5. Autogenous Deformation Versus Degree of Hydration as A Function of Cement Fineness for Cement Pastes With *w/c* = 0.35, Cured at 30°C (Bentz et al. 2001). Deformation Values Were Zeroed at the Setting Time (Degree of Hydration) of Each Cement Paste.

has been observed to re-percolate capillary pore networks that were originally depercolated by hydration products (Bentz 2006b).

4.0 MITIGATION STRATEGIES

4.1 Mixture Proportioning

The semi-adiabatic temperature rise and autogenous deformation experienced by a concrete mixture are strongly dependent on the interparticle spacing and the surface area of the cementitious binder that is exposed to water (Bentz, Sant & Weiss 2008; Bentz & Peltz 2008). Since the 1950s, the general trends in cement production have been to manufacture finer cements with higher tricalcium silicate (and possibly tricalcium aluminate) contents and a generally increased alkali content (Bentz, Sant & Weiss 2008; Tennis & Bhatty 2005). Each of these changes contributes to an increased reactivity at early ages, increasing the semi-adiabatic temperature rise and likely also the temperature gradient across a concrete member. The increase in fineness also decreases the interparticle spacing resulting in increased autogenous deformation, particularly in lower w/c mixtures.

Increased reactivity at early ages will also increase autogenous shrinkage, as less time is available for the beneficial effects of creep and stress relaxation to partially offset the autogenous stresses and strains. With ASTM Type IV (low heat of hydration) cements no longer available in the U.S. State departments of transportation and other concrete specifiers are basically limited to requesting the optional heat of hydration limit provided as part of the ASTM C150 specification for Type II cements if a reduced heat generation (reactivity) at early ages is desired or deemed necessary.

As indicated in Table 2, modifications to the mixture proportions can reduce both the semi-adiabatic temperature rise and the net autogenous deformation. Increasing the *w/c* from 0.35 to 0.4, switching to a coarser cement, or replacing a portion of the cement with a coarse limestone are each effective in accomplishing this objective. However, in each case, there is a concurrent reduction in 28 d strength, as increased (early-age) strength and a reduced probability for early-age cracking are often conflicting performance goals that must be carefully balanced in an appropriate design of a concrete

Table 2. Relative Mortar Cube Compressive Strength at 28 d, Maximum Temperature Achieved in Semi-Adiabatic Testing of Pastes, and (ε_{min}-ε_{max}) at 7 d for Mortars (Bentz & Peltz 2008).

Cement Paste or Mortar	Relative Strength at 28 d	Maximum Temperature (% Reduction vs. Control)	Autogenous Shrinkage (ε_{min}-ε_{max}) at 7 d and (% Reduction vs. Control)
w/c = 0.35 fine cement	100 %	66.9 °C (---)	-127 microstrains (---)
w/c = 0.35 coarse cement	74 %	47.4 °C (43 %)	-49 microstrains (61 %)
w/c = 0.40 fine cement	93 %	59.8 °C (16 %)	-100 microstrains (21 %)
w/cm = 0.357 fine cement/10 % fine limestone	93 %	58.8 °C (18 %)	-163 microstrains (-28 %)
w/cm = 0.357 fine cement/10 % coarse limestone	93 %	57.8 °C (20 %)	-88 microstrains (31 %)

mixture. While not included in the study in the Bentz & Peltz 2008 study, high volume fly ash mixtures that slowly hydrate and develop strength can also substantially reduce semi-adiabatic temperature rise and early-age autogenous shrinkage (Mehta 2004; Houk, Borge & Houghton 1969).

4.2 Reduction of Temperature Rise and Thermal Gradients

A variety of proven technologies are available for reducing the maximum temperature rise and temperature gradients in mass concrete construction including; the use of ice as part of the mixing water, chilled aggregates, cooling pipes, night time pours, insulating blankets, fly ash additions, and the incorporation of phase change materials into the concrete mixture (Mihashi et al. 2002). These approaches generally reduce the hydration rates or increase the thermal capacity of the concrete such that the heat generated by the hydration reactions results in a smaller temperature rise within the concrete member.

4.3 Shrinkage-Reducing Admixtures

Traditionally employed to reduce drying shrinkage, shrinkage-reducing admixtures (SRAs) have also proven effective in reducing plastic (Lura et al. 2007)

and autogenous shrinkage (Bentz, Geiker & Hansen 2001; Bentz 2006a). These chemical admixtures reduce the surface tension of the pore solution by up to a factor of two, resulting in a proportional decrease in capillary stresses according to equation (4). Generally, they also significantly increase the viscosity of the pore solution, which can improve durability and increase service life by reducing transport by diffusion, sorption, and/or flow under pressure (Bentz et al. 2008; Bentz et al. 2009).

Figure 6 provides an example of the measured reduction in autogenous deformation produced by the incorporation of an SRA into a mortar cured under sealed conditions. In this case, the reduction in autogenous shrinkage is basically proportional to the reduction in surface tension achieved by the addition of 2% SRA by mass of cement. For certain cements, SRAs may also increase the autogenous expansion that is produced at early-ages (Weiss et al. 2008), further reducing the measured absolute shrinkage at later ages. However, it must be kept in mind that it is the net shrinkage (following any early-age expansion) that is most relevant for determining whether autogenous shrinkage cracking may occur (Cusson 2008).

Expansive cements are another viable approach for offsetting early-age shrinkage. Such cements may be
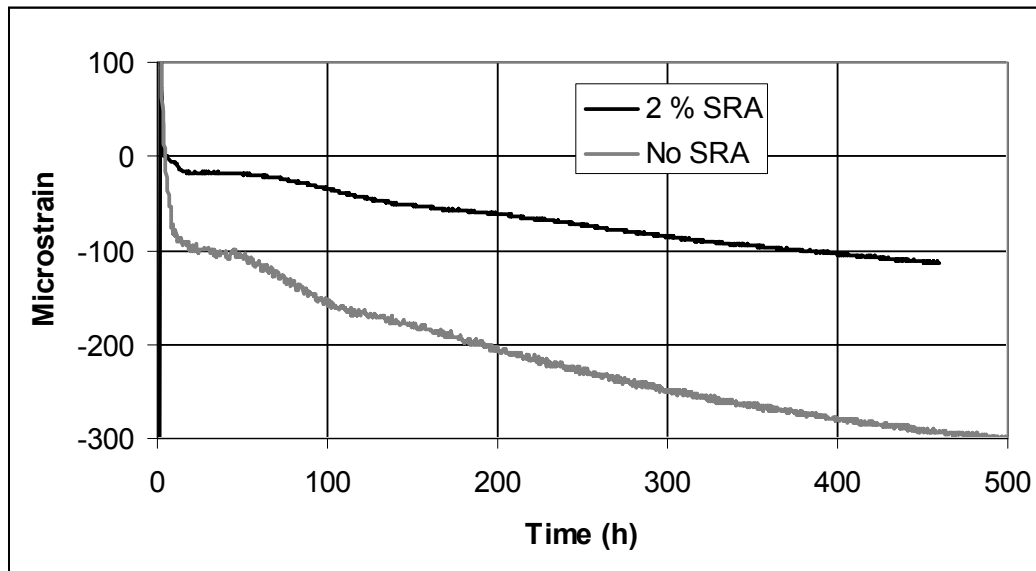
Figure 6. Differences In Autogenous Deformation (Measured Using the Experimental Setup of Jensen & Hansen 1995b) for Cement Mortars (*w/cm* = 0.35) With and Without SRA, Cured Under Sealed Conditions at 30ºC (Bentz, Geiker & Hansen 2001).

either shrinkage-compensating or self-stressing. In the former case, the goal is to use the expansion to balance the shrinkage in order to prevent cracking. In the latter case, larger expansions are generated to actually stress the concrete internally provided that there is restraint to the expansion. Several thousands microstrain of expansion in concrete can be produced by using expansive cements (Nagataki & Gomi 1998). The most common method of producing an expansive cement is via the formation of ettringite. There are several additions that can be used to increase ettringite formation in a portland cement, including calcium aluminate cements or $C_4A_3\bar{S}$.

It is generally accepted that in these cements, expansion is due to forces generated during the growth of preferentially oriented ettringite crystals. Other possibilities for producing expansive cements are via the hydration of free lime (*CaO*) or periclase (*MgO*) (Taylor 1997). In practice, expansive cements are sometimes difficult to regulate and control as the

expansion produced will depend on the reactivity of the expansive components and their spatial distribution within the cement powder. Thus, while self-desiccation is generally uniform throughout a concrete (due to the continuity of the water phase), expansion due to ettringite crystal formation, for example, can be a highly localized phenomena, due to the discrete nature of the growing crystals (Bentz et al. 2001).

4.4   Internal Curing

A careful examination of equation (4) indicates another viable approach to reducing early-age autogenous deformation: increasing the size of the pores that are emptied during self-desiccation by providing a sacrificial set of large initially-water-filled pores. These water reservoirs are typically provided by pre-wetted light weight aggregates (LWA) (Philleo 1991; Weber & Reinhardt 1995), superabsorbent polymers (Jensen & Hansen 2001; Jensen & Hansen

2002), pre-wetted wood fibers (Mohr et al. 2005), or pre-wetted crushed returned concrete aggregates (Kim & Bentz 2008). In the U.S., internal curing via LWA has been employed in several large scale concrete projects including a railway distribution yard (Villarreal & Crocker 2007), several bridge decks (Delatte et al. 2008), and a pavement (Friggle & Reeves 2008).

As mentioned earlier, 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. For LWA reservoirs, this amount can be calculated according to (Bentz, Lura & Roberts 2005):

$$M_{LWA} = \frac{C_f(CS)\alpha_{max}}{S\phi_{LWA}} \tag{6}$$

where:

MLWA is the mass of (dry) LWA needed per unit volume of concrete (kg/m^3 or lb/yd^3), C_f is the cement factor (content) for concrete mixture (kg/m^3 or lb/yd^3),
CS is the chemical shrinkage of cement (grams of water/gram of cement or lb/lb) at a degree of hydration equal to 100%,
α_{max} is the maximum expected degree of hydration of cement,
S is the degree of saturation of aggregate (0-1), and
ϕ_{LWA} is the absorption of lightweight aggregate (kg water/kg dry LWA or lb/lb), or more appropriately desorption from saturated surface dry conditions down to about 93% RH.

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 (Bentz & Snyder 1999; van Breugel & Lura 2000). A hard core/soft shell (HCSS) continuum microstructure model can be conveniently applied to quantifying this distribution and the "protected" paste volume for internal curing (Bentz & Snyder 1999; Bentz, Garboczi & Snyder 1999).

Figure 7 provides an indication of the reduction in autogenous deformation that is obtained when internal curing is used in a series of high performance blended cement mortars (Bentz 2007b). For systems with substantial pozzolanic reactions, such as those with silica fume and fly ash, IC may not totally eliminate autogenous shrinkage as some of this shrinkage may be due to the dissolution (and loss of micro-reinforcement) of calcium hydroxide crystals participating in the pozzolanic reactions with the mineral admixtures (Bentz & Stutzman 1994). For pure portland cement mixtures or those with a more hydraulic slag (as indicated in Figure 7), the autogenous deformation can be effectively totally eliminated by the appropriate addition of pre-wetted LWA.

Comprehensive information on internal curing will soon be available in a guide on the topic that is being prepared by ACI Committee 308 – Curing Concrete. To date, the most comprehensive review was that provided by Hoff (Hoff 2002). In addition, a comprehensive bibliography on internal curing is available via the Internet (*Internal Curing of Concrete 2009*). Recent results have indicated that internal curing can also be an effective means of reducing plastic shrinkage cracking, in addition to its well established reductions in autogenous deformation (Henkensiefken et al. 2009).
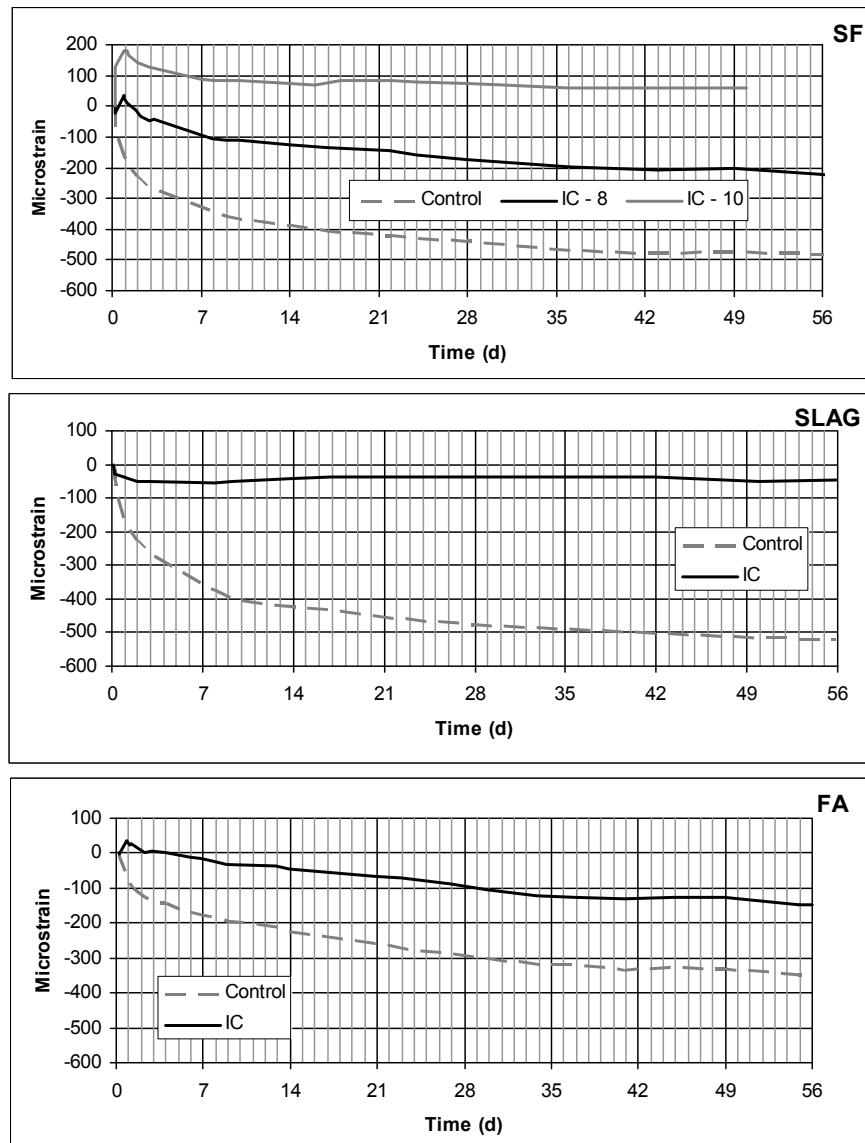
Figure 7. Autogenous Deformation of the Blended Cement Mortars: 8% Mass Fraction Silica Fume (SF) (top), 20% Mass Fraction Slag (middle), and 25% Mass Fraction Type F Fly Ash (FA) (bottom) During 56 d of Sealed Hydration at 25°C (Bentz 2007b). (For the SF System, IC-8 and IC-10 Indicate Internal Curing Additions of 0.08 and 0.10 Mass Units of Water Per Mass Unit of Cement, Respectively.)

5.0 REFERENCES

ACI Committee 231 State-of-the-Art Report, "Early-Age Cracking: Causes, Measurement, and Mitigation," American Concrete Institute, Farmington Hills, MI, 2009.

Andrade, C, Sarria, J, & Alonso, C 1999, "Relative Humidity in the Interior of Concrete Exposed to Natural and Artificial Weathering, *Cement and Concrete Research*, vol. 29, pp. 1249-1259.

ASTM C186-05, Standard Test Method for Heat of Hydration of Hydraulic cCement, Volume 04.01, ASTM International, West Conshohocken, PA, 2005.

ASTM C1608-06, Test Method for Chemical Shrinkage of Hydraulic Cement Paste, Volume 04.01, ASTM International, West Conshohocken, PA, 2006.

Barcelo, L, Boivin, S, Rigaud, S, Acker, P, Clavaud, B, & Boulay, C 1999, "Linear vs. Volumetric Autogenous Shrinkage Measurement: Material Behaviour or Experimental Artefact?," in Proceedings of the 2nd International Seminar on Self-Desiccation and Its Importance in Concrete Technology, B. Persson, G. Fagerlund (Eds.), Lund University, Lund, Sweden, pp. 109-125.

Baroghel-Bouny, V 1997, "Experimental Investigation of Self-desiccation in High-performance Materials – Comparison with Drying Behaviour," in Self-Desiccation and Its Importance in Concrete Technology, Proceedings of the 1st International Seminar, Report TVBM-3075, B. Persson and G. Fagerlund, Eds., Lund University, Lund, Sweden pp. 72-87.

Bensted, J. 1981, "Hydration of Portland Cement," Advances in Cement Technology, S. N. Ghosh, ed., Pergamon Press, New York, pp. 307-347.

Bentz, DP & Garboczi, EJ 1991, "Percolation of Phases in a Three-dimensional Cement Paste Microstructure Model," *Cement and Concrete Research*, vol. 21, no. 2, pp. 325-244.

Bentz, DP & Stutzman, PE 1994, "Evolution of Porosity and Calcium Hydroxide in Laboratory Concretes Containing Silica Fume," *Cement and Concrete Research*, vol. 24, no. 6, pp. 1044-50.

Bentz, DP 1997, "Three-dimensional Computer Simulation of Portland Cement Hydration and Microstructure Development," *Journal of the American Ceramic Society*, vol. 80, no. 1, pp. 3-21.

Bentz, DP, Garboczi, EJ, & Quenard, DA 1998, "Modeling Drying Shrinkage in Reconstructed Porous Materials: Application to Porous Vycor Glass," *Modeling and Simulation in Materials Science and Engineering*, vol. 6, no. 3, pp. 211-236.

Bentz, DP, Waller, V, & De Larrard, F 1998, "Prediction of Adiabatic Temperature Rise in Conventional and High-Performance Concretes Using a 3-D Microstructural Model," *Cement and Concrete Research*, vol. 28, no. 2, pp. 285-297.

Bentz, DP, Garboczi, EJ, & Snyder, KA 1999, "A Hard Core/Soft Shell Microstructural Model for Studying Percolation and Transport in Three-Dimensional Composite Media," NISTIR **6265**, U.S. Department of Commerce.

Bentz, DP & Snyder, KA 1999, "Protected Paste Volume in Concrete: Extension to Internal Curing using Saturated Lightweight Fine Aggregates," *Cement and Concrete Research*, vol. 29, pp. 1863-1867.

Bentz, DP, Geiker, MR, & Hansen, KK 2001, "Shrinkage-Reducing Admixtures and Early Age Desiccation in Cement Pastes and Mortars," *Cement and Concrete Research*, vol. 31, no. 7, pp. 1075-1085.

Bentz, DP, Jensen, OM, Hansen, KK, Oleson, JF, Stang, H, & Haecker, CJ 2001, "Influence of Cement Particle Size Distribution on Early Age Autogenous Strains and Stresses in Cement-based Materials," *Journal of the American Ceramic Society*, vol. 84, no. 1, pp. 129-135.

Bentz, DP, Lura, P, & Roberts, JW 2005, "Mixture Proportioning for Internal Curing," *Concrete International*, 27 (2), 35-40.

Bentz, DP 2006a, "Influence of Shrinkage-Reducing Admixtures on Drying, Autogenous Shrinkage, and Freezable Water Content of Cement Pastes at Early Ages," *Journal of Advanced Concrete Technology*, vol. 4, no. 3, pp. 423-429.

Bentz, DP 2006b, "Capillary Porosity Depercolation/ Repercolation in Hydrating Cement Pastes via Low Temperature Calorimetry Measurements and CEMHYD3D Modeling," Journal of the American Ceramic Society, vol. 89, no. 8, pp. 2606-2611.

Bentz, DP 2007a, "Transient Plane Source Measurements of the Thermal Properties of Hydrating Cement Pastes," *Materials and Structures*, vol. 40, no. 12, pp. 1073-1080.

Bentz, DP 2007b, "Internal Curing of High Performance Blended Cement Mortars," *ACI Materials Journal*, vol. 104, no. 4, pp. 408-414.

Bentz, DP 2007c, "Verification, Validation, and Variability of Virtual Standards," 12th International Congress on the Chemistry of Cement, Montreal.

Bentz, DP 2008, "A Review of Early-Age Properties of Cement-Based Materials," *Cement and Concrete Research*, vol. 38, no. 2, pp. 196-204.

Bentz, DP & Aitcin, P-C 2008, "The Hidden Meaning of Water-to-Cement Ratio," *Concrete International*, vol. 30, no. 5, pp. 51-54.

Bentz, DP & Peltz, MA 2008, "Reducing Thermal and Autogenous Shrinkage Contributions to Early-Age Cracking," *ACI Materials Journal*, vol. 105, no. 4, pp. 414-420.

Bentz, DP, Sant, G, & Weiss, WJ 2008, "Early-Age Properties of Cement-Based Materials: I. Influence of Cement Fineness," *ASCE Journal of Materials in Civil Engineering*, vol. 20, no. 7, pp. 502-508.

Bentz, DP, Snyder, KA, Cass, LC, & Peltz, MA 2008, "Doubling the Service Life of Concrete. I: Reducing Ion Mobility Using Nanoscale Viscosity Modifiers," *Cement and Concrete Composites*, vol. 30, pp. 674-678.

Bentz, DP, Peltz, MA, Snyder, KA, & Davis, JM 2009, "VERDiCT: Viscosity Enhancers Reducing Diffusion in *Concrete Technology*," Concrete International, vol. 31, no. 1, pp. 31-36.

Bjontegaard, O 1999, "Thermal Dilation and Autogenous Deformation as Driving Forces to Self-induced Stresses in High Performance Concrete," Ph.D. Thesis, Norweigan University of Science and Technology, Norway.

Bouguerra, A, Laurent, JP, Goual, MS, & Queneudec, M 1997, "The Measurement of the Thermal Conductivity of Solid Aggregates Using the Transient Plane Source Technique," *Journal of Physics D: Applied Physics*, vol. 30, pp. 2900-2904.

Brown, K, Brown, AW, Colpitts, BG, & Bremner, TW 2004, "The Mitigation of Measurement Inaccuracies of Brillouin Scattering Based Fiber Optic Sensors Through Bonded Fiber Temperature Calibrations," in *Proceedings of the 7th Cansmart Workshop: Smart Materials and Structures*, Montreal, Quebec, Canada, pp. 317-324.

Cusson, D 2005, "Early-Age Cracking of Concrete in Bridge Barrier Walls," NRC-IRC, available at http://irc.nrc-cnrc.gc.ca/ui/cs/earlyage_e.html (access verified February 2009).

Cusson, D 2008, "Effect of Blended Cements on Efficiency of Internal Curing of HPC," in ACI SP-256, *Internal Curing of High-Performance Concretes: Laboratory and Field Experiences*, American Concrete Institute, Farmington Hills, MI, CD-ROM, pp. 105-120.

Delatte, N, Crowl, D, Mack, E, & Cleary, J 2008, "Evaluating High Absorptive Materials to Improve Internal Curing of Concrete," in *ACI SP-256, Internal Curing of High-Performance Concretes: Laboratory and Field Experiences*, American Concrete Institute, Farmington Hills, MI, pp. 91-104.

Durán-Herrera, A, Petrov, N, Bonneau, D, Khayat, K, & Aitcin, PC 2008, "Autogenous Control of Autogenous Shrinkage," in *ACI SP-256, Internal Curing of High-Performance Concretes: Laboratory and Field Experiences*, American Concrete Institute, Farmington Hills, MI, CD-ROM, pp. 1-12.

Friggle, T & Reeves, D 2008, "Internal Curing of Concrete Paving: Laboratory and Field Experience," in *ACI SP-256, Internal Curing of High-Performance Concretes: Laboratory and Field Experiences*, American Concrete Institute, Farmington Hills, MI, pp. 71-80.

Fukuhara, M, Goto, S, Asaga, K, Daimon, M, & Kondo, R 1981, "Mechanisms and Kinetics of C4AF Hydration with Gypsum," *Cement and Concrete Research*, vol. 11, pp. 407-414.

Geiker, MR 1983, "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.

Grasley, ZC, Lange, DA, Brinks, AJ, & D'Ambrosia, MD 2005, "Modeling Autogenous Shrinkage of Concrete Accounting for Creep Caused by Aggregate Restraint," in *Proceedings of the 4th International Seminar on Self-Desiccation and Its Importance in Concrete Technology*, B. Persson, D. Bentz, L.-O. Nilsson (Eds.), NIST, Gaithersburg, MD, pp. 78-94.

Grasley, ZC, D'Ambrosia, MD, & Lange, DA 2006, "Internal Relative Humidity and Drying Stress Gradients in Concrete," *Materials and Structures*, vol. 39, no. 9, pp. 901-909.

Hammer, TA & Heese, C 1999, "Early Age Chemical Shrinkage and Autogenous Deformation of Cement Pastes," in Proceedings of the 2nd International Seminar on Self-Desiccation and Its Importance in Concrete Technology, B. Persson, G. Fagerlund (Eds.), Lund University, Lund, Sweden, pp. 7-13.

Hashin, Z & Shtrikman, S 1962, "A Variational Approach to the Theory of the Effective Magnetic Permeability of Multiphase Materials," *Journal of Applied Physics*, vol. 33, pp. 3125-3131.

Henkensiefken, R, Briatka, P, Bentz, D, Nantung, T, & Weiss, J 2009, "Plastic Shrinkage Cracking in Internally Cured Mixtures Made with Pre-wetted Lightweight Aggregate," submitted to *Concrete International*.

Hoff, GC 2002, "The Use of Lightweight Fines for Internal Curing of Concrete," Northeast Solite Corporation, 44 pp, available at http://www.nesolite.com/Reports/solitepaper.pdf, access verified September 2008.

Horai, K 1971, "Thermal Conductivity of Rock-Forming Minerals," *Journal of Geophysical Research*, vol. 76, no. 5, pp. 1278-1308.

Houk, IE, Borge, OE, & Houghton, DR 1969, "Studies of Autogenous Volume Change in Concrete for Dworshak Dam," *ACI Journal*, vol. 66, no. 5, pp. 560-568.

Hua, C, Acker, P, & Erlacher, A 1995, "Analyses and Models of the Autogenous Shrinkage of Hardening Cement Pastes," *Cement and Concrete Research*, vol. 25, no. 7, pp. 1457-1468.

Internal Curing of Concrete, at http://ciks.cbt.nist.gov/~bentz/phpct/database/ic.html, access verified April 2009.

Jensen, OM 1990, "The Pozzolanic Reaction of Silica Fume," M.S. Thesis, Technical Report TR229/90, Technical University of Denmark, Lyngby, Denmark, (in Danish).

Jensen, OM & Hansen, PF 1995a, "Autogenous Relative Humidity Change in Silica Fume-modified Cement Paste," *Advances in Cement Research*, vol. 7, no. 25, pp. 33-38.

Jensen, OM & Hansen, PF 1995b, "A Dilatometer for Measuring Autogenous Deformation in Hardening Portland Cement Paste," *Materials and Structures*, vol. 28, no. 181, pp. 406-409.

Jensen, OM & Hansen, PF 1996, "Autogenous Deformation and Change of the Relative Humidity in Silica Fume-modified Cement Paste," *ACI Materials Journal*, vol. 93, no. 6, pp. 539-543.

Jensen, OM, Hansen, PF, Lachowski, EE, & Glasser, FP 1999, "Clinker Mineral Hydration at Reduced Relative Humidities," *Cement and Concrete Research*, vol. 29, no. 9, pp. 1505-1512.

Jensen, OM & Hansen, PF 2001, "Water-entrained Cement-based Materials I. Principles and Theoretical Background," *Cement and Concrete Research*, vol. 31, no. 4, pp. 647-654.

Jensen, OM & Hansen, PF 2002, "Water-entrained Cement-based Materials: II. Experimental Observations," *Cement and Concrete Research*, vol. 32, no. 6, pp. 973-978.

Justnes, H, Sellevold, EJ, Reyniers, B, Van Loo, D, Van Gemert, A, Verboven, F, & Van Gemert, D 1999, "The Influence of Cement Characteristics on Chemical Shrinkage," in Autogenous Shrinkage of Concrete, E. Tazawa (Ed.), E&FN Spon, London, pp. 71-80.

Kim, K-H, Jeon, S-E, Kim, J-K, & Yang, S 2003, "An Experimental Study on Thermal Conductivity of Concrete," *Cement and Concrete Research*, vol. 33, pp. 363-371.

Kim, H & Bentz, DP 2008, "Internal Curing with Crushed Returned Concrete Aggregates," in *NRMCA Technology Forum: Focus on Sustainable Development*, CD-RoM.

Kishi, T., and Maekawa, K. 1995, "Thermal and Mechanical Modeling of Young Concrete Based on Hydration Process of Multi-Component Cement Minerals," Proceedings of the International RILEM Symposium on Thermal Cracking in Concrete at Early Ages, R. Springenschmid, ed., E&FN Spon, London, pp. 11-18.

Lee, KM, Lee, HK, Lee, SH, & Kim, GY 2006, "Autogenous Shrinkage of Concrete Containing Granulated Blast-furnace Slag," *Cement and Concrete Research*, vol. 36, no. 7, pp. 1279-1285.

Lura, P, Jensen, OM, & van Breugel, K 2003, "Autogenous Shrinkage in High-performance Cement Paste: An Evaluation of Basic Mechanisms," *Cement and Concrete Research*, vol. 33, no. 2, pp. 223-232.

Lura, P & Jensen, OM 2005, "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.

Lura, P, Pease, B, Mazzotta, G, Rajabipour, F, & Weiss, J 2007, "Influence of Shrinkage-Reducing Admixtures on the Development of Plastic Shrinkage Cracks," *ACI Materials Journal*, vol. 104, no. 2, pp. 187-194.

MacKenzie, JK 1950, "The Elastic Constants of a Solid Containing Spherical Holes," *Proceedings of the Physical Society*, vol. 683, pp. 2-11.

Maekawa, K, Chaube, R, & Kishi, T (Eds.) 1999, Modelling of Concrete Performance: Hydration, Microstructure Formation, and Mass Transport, E&FN Spon, London.

McCullough, BF & Rasmussen, RO 1999, "Fast-track Paving: Concrete Temperature Control and Traffic Opening Criteria for Bonded Concrete Overlays, FHWA-RD-98-167.

McGrath, P & Hooton, RD 1991, "Self-desiccation of Portland Cement and Silica Fume Modified Mortars," in Ceramic Transactions, Vol. 16, Advances in Cementitious Materials, S. Mindess (Ed.), The American Ceramic Society, Inc., Westerville, OH, pp. 489-500.

Mehta, PK 2004, "High-Performance, High-Volume Fly Ash Concrete For Sustainable Development," in *Proceedings of the International Workshop on Sustainable Development and Concrete Technology*, Beijing, China, pp. 3-14.

Mihashi, H, Nishiyama, N, Kobayashi, T, & Hanada, M 2002, "Development of a Smart Material to Mitigate Thermal Stress in Early Age Concrete," in *Control of Cracking in Early Age Concrete*, Eds. H. Mihashi & F. H. Wittmann, Balkema, Rotterdam, pp. 385-392.

Mohr, B, Premenko, L, Nanko, H, & Kurtis, KE 2005, "Examination of Wood-derived Powders and Fibers for Internal Curing of Cement-based Materials," in *Proceedings of the 4th International Seminar on Self-Desiccation and Its Importance in Concrete Technology*, B. Persson, D. Bentz, L.-O. Nilsson (Eds.), NIST, Gaithersburg, MD, pp. 229-244.

Moon, J-H, Rajabipour, F, Pease, B, & Weiss, WJ 2005, "Autogenous Shrinkage, Residual Stress, and Cracking in Cementitious Composites: The Influence of Internal and External Restraint," in *Proceedings of the 4th International Seminar on Self-Desiccation and Its Importance in Concrete Technology*, B. Persson, D. Bentz, L.-O. Nilsson (Eds.), NIST, Gaithersburg, MD, pp. 1-20.

Mounanga, P, Khelidj, A, Loukili, A, & Baroghel-Bouny, V 2005, "Predicting Ca(OH)2 Content and Chemical Shrinkage of Hydrating Cement Pastes using Analytical Approach," *Cement and Concrete Research*, vol. 34, no. 2, pp. 255-265. Erratum published in Cement and Concrete Research, vol. 35, pp. 423-424.

Nagataki, S. and Gomi, H. 1998. "Expansive Admixtures." *Cement and Concrete Composites*, vol. 20. pp. 163-170.

Persson, B. and Fagerlund, G. (Eds.) 1997, Self-Desiccation and Its Importance in Concrete Technology 1997, Proceedings of the 1st International Seminar, Report TVBM-3075, Lund University, Lund, Sweden.

Philleo, RE 1991, "Concrete Science and Reality," in Materials Science of Concrete II, J. Skalny, S. Mindess (Eds.), American Ceramic Society, Westerville, OH, pp. 1-8.

Poppe, AM, & De Schutter, G 2006, "Analytical Hydration Model for Filler Rich Self-Compacting Concrete," J*ournal of Advanced Concrete Technology*, vol. 4, no. 3, pp. 259-266.

Powers, TC 1935, "Adsorption of Water by Portland Cement Paste during the Hardening Process," *Industrial and Engineering Chemistry*, vol. 27, pp. 790-794.

Powers, TC, Copeland, LE, & Mann, HM 1959, "Capillary Continuity or Discontinuity in Cement Paste," PCA Bulletin No. 10, pp. 2-12.

Roelfstra, PE, Salet, TAM, & Kuiks, JE 1994, "Defining and Application of Stress-analysis-based Temperature Difference Limits to Prevent Early-age Cracking in Concrete Structures," in *Proceedings of the International RILEM Symposium: Thermal Cracking in Concrete at Early Ages*, Munich, pp. 273-280.

Ruiz, JM, Rasmussen, RO, Chang, GK, Dick, JC, & Nelson, PK 2005, "Computer-based Guidelines for Concrete Pavements Volume II – Design and Construction Guidelines and HIPERPAV II User's Manual," FHWA-HRT-04-122.

Taylor, HFW 1997, Cement Chemistry 2nd edition, Thomas Telford, London.

Tazawa, E., (Ed.) 1999, Autogenous Shrinkage of Concrete, E&FN Spon, London, pp. 53-55.

Tennis, PD & Bhatty, JI 2005, "Portland Cement Characteristics-2004." *Concrete Technology Today*, Portland Cement Association, vol. 26, no. 3, pp. 1-3.

van Breugel, K & Lura, P 2000, "Effect of Initial Moisture Content and Particle Size Distribution of Lightweight Aggregates on Autogenous Deformation," in: Proceedings of the 2nd International Symposium on Structural Lightweight Concrete, S. Helland, I. Holand, S. Smeplass (Eds.), Kristiansand, Norway, pp. 453-462.

Villarreal, V & Crocker, D 2007, "Building Better Pavements through Internal Hydration," *Concrete International*, vol. 29, no. 2, pp. 32-36.

Viviani, M, Glisic, B, & Smith, IFC 2007, "Separation of Thermal and Autogenous Deformation at Varying Temperature using Optical Fiber Sensors," *Cement and Concrete Composites*, vol. 29, pp. 435-447.

Vosteen, H-D & Schellschmidt, R 2003, "Influence of Temperature on Thermal Conductivity, Thermal Capacity, and Thermal Diffusivity for Different Types of Rocks," *Physics and Chemistry of the Earth*, vol. 28, pp. 499-509.

Wadso, L 2002, "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.

Waller, V, De Larrard, F, & Roussel, P 1996, "Modelling the Temperature Rise in Massive HPC Structures," in *4th International Symposium on Utilization of High-Strength/High-Performance Concrete*, RILEM S.A.R.L., Paris, pp. 415-421.

Weber, S & Reinhardt, HW 1995, "A Blend of Aggregates to Support Curing of Concrete," in *Proceedings of the International Symposium on Structural Lightweight Aggregate Concrete*, I. Holand, T.A. Hammer, P. Fluge (Eds.), Sandefjord, Norway, pp. 662-671.

Weiss, J, Lura, P, Rajabipour, F, & Sant, G 2008, "Performance of Shrinkage Reducing Admixtures at Different Humidities and at Early Ages," *ACI Materials Journal*, vol. 105, no. 5, pp. 478-486.