

Volume Changes in Pastes Containing Shrinkage Reducing Admixtures under Autogenous and Drying Conditions

G. Sant¹, F. Rajabipour¹, A. Radlinska¹, P. Lura², W.J. Weiss¹

¹Purdue University, West Lafayette, Indiana, USA

²European Patent Office, Munich, Germany

A new class of chemical admixtures, commonly referred to as shrinkage reducing admixtures or SRAs, has been developed over the past two decades to reduce the potential for early age cracking in concrete facilities. While a substantial number of experimental results have been presented in the literature to demonstrate how SRA's influence the free shrinkage of cementitious mixtures tested in accordance with ASTM C-157, substantially fewer results have shown the influence of SRA on volume changes that occur from the time of casting till the standard shrinkage tests begin. Even fewer tests have been conducted in environments other than 50% relative humidity. This paper discusses both the initial (i.e., measured from the time of casting) and long-term shrinkage behavior of four cement paste systems over a wide range of relative humidities in a CO₂ free environment.

1. Introduction

Over the last two decades, substantial research has been conducted to assess the performance of shrinkage reducing admixtures (SRA) in cement pastes, mortars, and concretes [1,2,3,4,5,6]. These works indicated that SRAs can be effective in reducing strains associated with drying shrinkage at early ages. Reductions in shrinkage have been related to a reduction in the surface tension of the pore fluid in mixtures containing SRA. The influence of SRA on the surface tension has been simulated using solutions of deionized water-SRA and pore-solution SRA mixtures [7,8,9]. The reduction in shrinkage strain also results in a reduction in the potential for restrained shrinkage cracking [2,3,6]

It has been reported that SRA's may reduce shrinkage from 30% up to 80% in concrete depending on mixture composition, curing and drying time [10]. In addition to measuring drying shrinkage and cracking, autogenous (sealed) shrinkage of specimens has also been measured [8,11,12]. Weiss et al. [11] demonstrated that SRA's reduce a greater proportion of shrinkage at early ages while Sant et al. [12] demonstrated that initiating shrinkage measurements at the time of set is essential as an expansion can occur at these early ages which would complicate the

interpretation of experimental results. Bentz [8] suggested that in addition to the decrease in surface tension, SRAs slow the rate of reduction in relative humidity of mixtures experiencing self-desiccation.

Researchers have measured moisture gradients in specimens where moisture decreases more rapidly at the surface than it does in the core of the concrete. Bentz [8] observed a substantial difference in the moisture gradients that develop in fresh (i.e., fluid) paste with and without SRA. Specimens containing SRA were noted to have a more uniform moisture distribution. Other studies have quantified moisture gradients in hardened concrete elements [13,14] and similar moisture profiles were obtained for plain concretes and concretes containing SRA. This moisture loss was described using Ficks Seconds Law [15]. The humidity profiles were related to shrinkage profiles using an approach described by L' Hermitte [16], Bazant [17], Weiss [18] and Pease [9]. This approach, described in Equation 1, relates relative humidity and shrinkage and employs Pickett's Model [19] to account for the influence of the aggregate on the shrinkage of the system.

$$e_{Concrete} = e_{Paste} \cdot (1 - V_F)^n = \beta_N \cdot (1 - RH^3) \cdot (1 - V_F)^n \quad \text{Equation 1}$$

where $\epsilon_{Concrete}$ is the shrinkage strain of the mortar or concrete ($\mu\text{m}/\text{m}$), ϵ_{Paste} is the shrinkage strain of the cement paste ($\mu\text{m}/\text{m}$), β_N is the hygral shrinkage coefficient of the system (non-linear with relative humidity), V_f is the volume fraction of aggregate in the system (unitless), RH is the ambient relative humidity of the environment (unitless), and n is a value between 1.2 and 1.7 (normal aggregate) and cement paste. Pease et al. [9] demonstrated that β_N could be related to the pore fluid surface tension.

Bentz et al. [20] used an alternative approach to describe the shrinkage response adapting a model originally developed by Mackenzie [21] for a fully saturated porous medium. Bentz et al. [20] proposed that a saturation factor could be added to account for partial saturation using Equation 2.

$$e = S \frac{\rho_{cap}}{3} \left(\frac{1}{K_P} - \frac{1}{K_S} \right) \quad \text{Equation 2}$$

where ϵ is the shrinkage of the material ($\mu\text{m}/\text{m}$), S [m^3 water / m^3 pore] is the saturation fraction, ρ_{cap} [MPa] is the capillary stress in the pore fluid, K_P [MPa] the bulk modulus of the whole porous body, and K_S [MPa] is the bulk modulus of the solid material, excluding the effect of the porosity.

2. Research Significance

While SRA's have been studied for nearly two decades, the majority of these studies have focused on the shrinkage response of these materials at 50% relative humidity. This paper examines the autogenous shrinkage of cement pastes containing SRA and the drying shrinkage of cement pastes over a wide range of relative humidities.

3. Materials and Methods

Four different cement paste mixtures were prepared according to the mixture proportions shown in Table 1. Type I ordinary portland cement was used with a Blaine fineness of 360 m²/kg and a Bogue phase composition of 60% C₃S, 12% C₂S, 12% C₃A, 7% C₄AF and a Na₂O equivalent of 0.72%. A commercially available undensified silica fume (Microsilica 965) manufactured by Elkem AS was added at 20% addition by weight of cement. The phase composition of the silica fume used was 93.0% SiO₂, 0.5% Fe₂O₃, 0.7% Al₂O₃, 0.7% CaO, 0.7% MgO, 0.9% K₂O and a Na₂O equivalent of 0.4%. The silica fume used has a density of 2.20 g/cm³. To enhance the workability and consistency of the mixture, a high range water reducer was added (Glenium 3000NS for plain pastes and PS-1232 for silica fume pastes). A shrinkage reducing admixture (Tetraguard AS20) was added at 1.5% of the weight of cement or a 5% concentration of the initial water-SRA solution by replacement (by weight) of the initial mixing water.

Table 1: Mixture Proportions and Mixing Procedures

	w/c = 0.30	w/c = 0.30 + 5% SRA	w/c = 0.30 + 20% SF	w/c = 0.30 + 20%SF +5% SRA
Water	0.300	0.285	0.300	0.285
Cement	1.000	1.000	1.000	1.000
Silica Fume	~	~	0.200	0.200
HRWRA	0.050	0.050	0.083	0.083
SRA	~	0.015	~	0.015

De-aired, neat cement paste was prepared using de-ionized water. The water was boiled to remove dissolved air and then cooled to room temperature prior to mixing. The dry constituent materials were placed inside a special mixing chamber [22]. The chamber was sealed; air was evacuated from the chamber using a vacuum pump, and the solution of

water and the chemical admixtures was introduced into the chamber under the same evacuated condition. The chamber was then placed in a commercial paint shaker and shaken for five minutes to uniformly mix the constituents and obtain a consistent cement paste mixture. After mixing, the chamber was opened and the cement paste slurry was placed in the molds using external vibration.

4. Specimen Preparation

This section describes procedures used in specimen preparation and conditioning. Three specimen geometries were prepared including specimens to measure: (1) autogenous strain of sealed samples (2) shrinkage strain and weight loss of drying samples, and (3) relative humidity measurements of sealed samples. The details are as follows:

4.1. Autogenous strain of sealed samples

Linear autogenous strain of cement pastes was measured in a technique where the fresh paste was placed in corrugated polyethylene molds with a length-to-diameter ratio of approximately 400:30 mm [23]. The technique is designed to encapsulate the fresh cement paste while minimizing restraint, thereby permitting measurements to start 30 minutes after water addition. The corrugated mold transforms volumetric deformations into linear deformations when the paste is in a fluid state, since the mold has a greater stiffness in the radial direction than in the longitudinal direction.

The cement paste was cast into the corrugated tubes and then vibrated. The specimen was then placed in a dilatometer which was maintained at $23\pm 1^\circ\text{C}$. The dilatometer was equipped with automatic data-logging and electronic linear displacement transducers; with a measuring accuracy of $\pm 5 \mu\text{m/m}$. The measurements were performed every 5 minutes and started at about 30 minutes after water addition.

4.2. Shrinkage strain of drying samples

Cylindrical cement paste specimens were prepared with a 12.5 mm (1/2 in.) diameter and 87 mm (3.4 in.) gage length. Embedded stainless steel screws were cast in the end of each specimen to enable comparator measurements. The paste mixtures were cast and kept in the sealed

forms for 24 hours at $23\pm 1^\circ\text{C}$. After demolding, the samples were sealed in plastic bags for an additional 6 days at $23\pm 1^\circ\text{C}$. At an age of 7 days the specimens were placed in computer controlled Vena VC-10 Environmental Chambers at a constant temperature of $23\pm 1^\circ\text{C}$ and varying RH values, including 95%, 87%, 70%, 50%, and 30% ($\pm 1\%$ RH).

4.3. Relative humidity of sealed samples

Fresh cement paste was cast in air-tight plastic vials which were sealed. At an age of 12 hours, 10 g of crushed cement paste was placed in a glass vial and the vial was then sealed to prevent moisture loss. The sealed glass vial was then immersed in a water bath to maintain thermal equilibrium. A Digitron 2080R temperature and relative humidity meter equipped with a Pt-100 temperature sensor and a capacitive RH sensor was used to record relative humidity and temperature data inside the sealed vial at intervals of 2 hours for a period of 7 days from the time of addition of water to dry cement. Before the measurements were performed, calibration of the sensor was carried out using saturated salt solutions (K_2SO_4 , KNO_3 , KCl , and NaCl) with known RH in the range 75-100% (ASTM E104) [24].

5. Experimental Results

5.1 Autogenous strain of sealed specimens

Figure 1 shows the typical strain response of sealed samples for the first 7 days. It was observed that for both mixtures, with or without silica fume, the addition of SRA results in an expansion that occurs after setting. Moreover, after the initial expansion, the SRA mixtures show a lower rate of shrinkage compared to the plain mixtures. This is consistent with the change in surface tension [9] and the decrease in the rate of reduction of relative humidity as observed by Bentz [8]. It should also be noted that the plain mixtures show a plateau in the development of shrinkage a few hours after setting. The SRA mixtures show an expansion a few hours after setting. The silica fume mixtures shrink more than the plain mixtures, while the majority of this shrinkage occurs between setting and 24 hours.

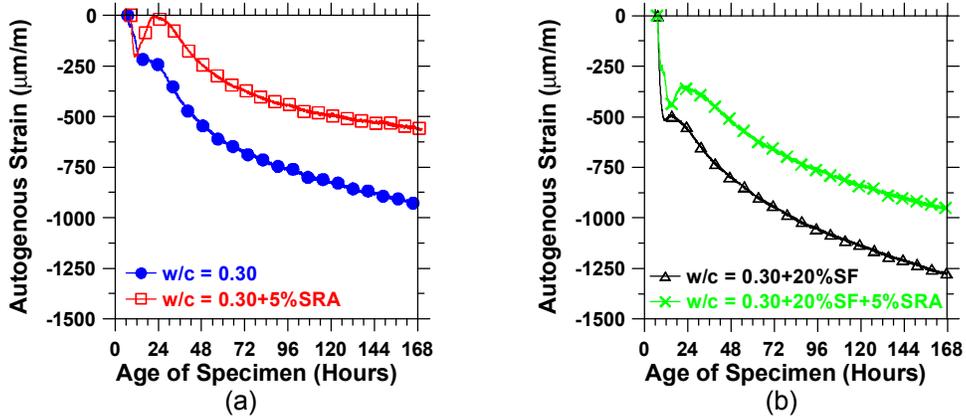


Figure 1: Autogenous Shrinkage Measured in a Sealed Specimen during the First 7 Days: a) $w/c = 0.30$ and $w/c = 0.30 + 5\% \text{ SRA}$ and b) $w/c = 0.30 + 20\% \text{ Silica Fume}$ and $w/c = 0.30 + 20\% \text{ Silica Fume} + 5\% \text{ SRA}$

5.2 Shrinkage strain and weight loss results of drying specimens

Figures 2 and 3 illustrate the weight change due to water loss and shrinkage strain that is measured at an age of 149 days (after 7 days sealed curing and 142 days of drying). The results shown are based on the average of three specimens.

Figure 2(a) indicates that addition of SRA does not appear to substantially alter the total amount of water that is lost (calculated as a weight change) from the specimens. This is consistent with earlier observations [18,25]. It should be noted however that the SRA appears to alter the rate of moisture loss (weight change) from the samples.

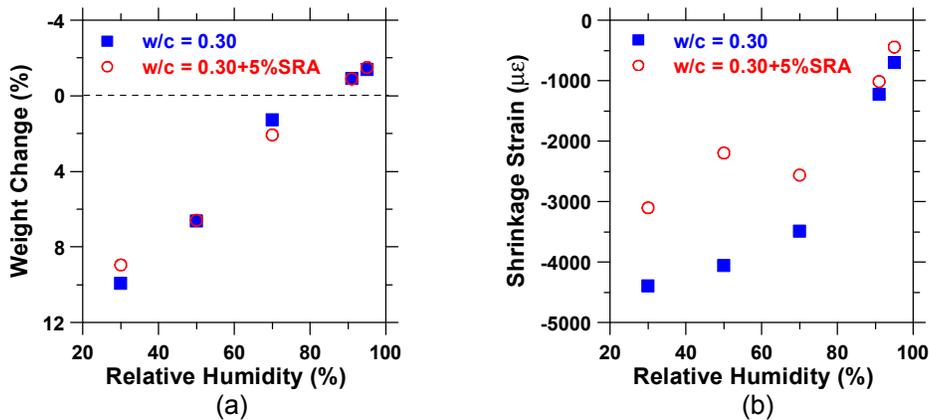


Figure 2: Weight change and Shrinkage measured in specimens exposed to drying after 7 Days: (a, b) $w/c = 0.30$ and $w/c = 0.30 + 5\% \text{ SRA}$

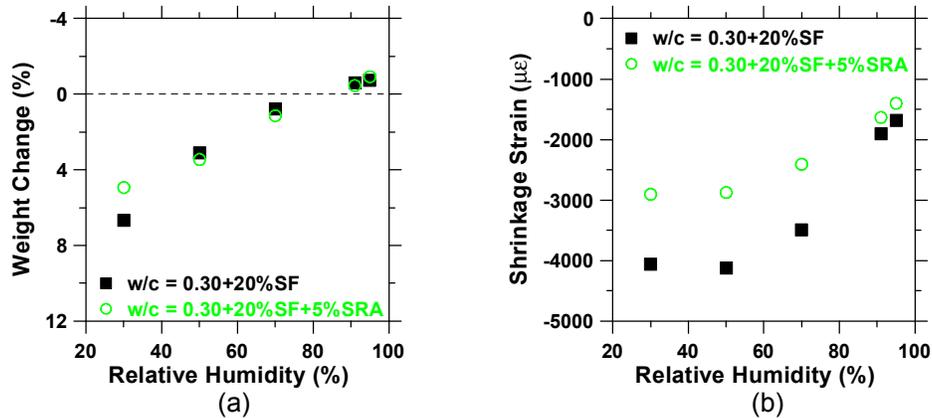


Figure 3: Weight change and Shrinkage measured in specimens exposed to drying after 7 Days: (a, b) $w/c = 0.30 + 20\%$ Silica Fume and $w/c = 0.30 + 20\%$ Silica Fume + 5% SRA

The plain cement pastes lose more water (6% weight loss at 50% RH) during drying than specimens containing Silica Fume (3% weight loss at 50% RH). This is consistent with the fact that mixtures containing silica fume have lower water content, since the water-binder ratio for these mixtures is 0.25. Specimens stored at 87% and 95% RH gained weight, suggesting that the internal relative humidity of a sealed sample is lower than these values. Data from Figures 2 and 3 suggests the internal relative humidity to be in the order of 80-85%.

Also Figure 2(b) and 3(b) show that the shrinkage of the mixtures containing SRA is substantially lower than the shrinkage of the plain pastes for specimens at low RH (70%, 50%, and 30%). However, these values are more similar for higher RH (87% and 95%).

5.3 Relative Humidity of Sealed Specimens

Figure 4 illustrates the RH measured from sealed specimens. The specimens containing silica fume have a more rapid reduction of the internal RH than the plain cement mixtures. The relative humidity decreases more rapidly in the plain cement mixtures than in the SRA mixtures. This is consistent with the observations of Bentz et al. [8] for a SRA system.

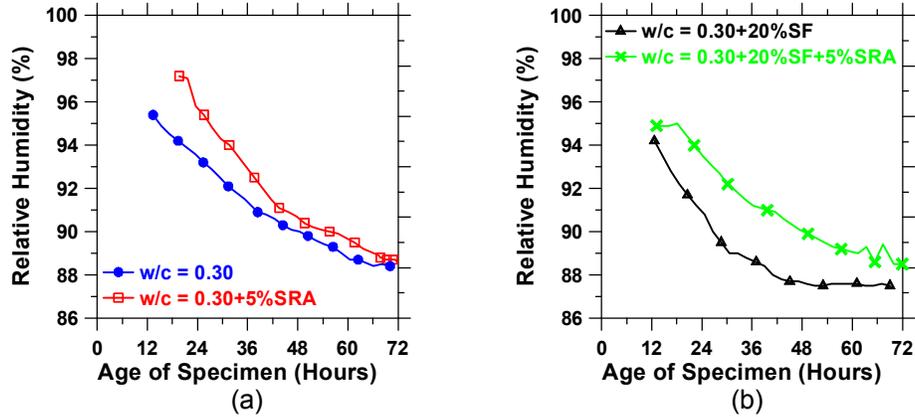


Figure 4: Relative humidity of sealed samples as a function of time: a) w/c = 0.30 and b) w/c = 0.30 + 20% Silica Fume

6. Discussion

Before beginning the discussion of results, it is important to review the relationships between relative humidity, surface tension and pore size.

The Kelvin Young Laplace equation can be used to determine the minimum pore radius that empties for a material at a specific relative humidity at a specific surface tension. Assuming the change in chemical composition is small and can be neglected on initial discussion (i.e., Raoult's Law).

$$r_K = \frac{-2\gamma V_w \cos \theta}{\ln(RH) \cdot R \cdot T} \quad \text{Equation 3}$$

where r_K [m] is the Kelvin radius, (i.e. the radius of the fluid-vapor menisci), RH is the partial vapor pressure of the pore fluid contained in the pores, V_w is the molar volume of the pore fluid, assumed equal to the molar volume of water, $18.02 \cdot 10^{-6} \text{ m}^3/\text{mol}$; θ [-] is the contact angle between pore fluid and solids; γ [N/m] is the surface tension of the pore fluid; R is the ideal gas constant, $8.314 \text{ J}/(\text{mol}\cdot\text{K})$; T [K] is the absolute temperature.

The surface tension in the pore fluid can be calculated for distilled water with SRA addition [9]:

$$\begin{aligned} g_{SOL} &= g_w \cdot \left[1 - d \cdot \ln\left(\frac{c_{SRA}}{f}\right) \right] & c_{SRA} < 15\% \\ g_{SOL} &= g_{SOL,SAT} & c_{SRA} \geq 15\% \end{aligned} \quad \text{Equation 4}$$

where, g_{SOL} [N/m] is the surface tension of the solution of distilled water and SRA, g_W [N/m] is the surface tension of the distilled water, C_{SRA} is the SRA content as wt.-% of water, $g_{SOL,SAT}$ [N/m] is the surface tension of the solution of distilled water and SRA at saturation, d [-] is a constant characteristic of a series of organic compounds similar in structure (i.e. SRA), and f [wt.-%] is a constant of an individual compound. Pease [9] determined that the surface tension plateaus beyond 15% addition of SRA (i.e., $g_{SOL,SAT}$ [N/m]). Pease [9] also tabulated the values for d , f , and $g_{SOL,SAT}$ for a number of SRAs. For the SRA (Tetraguard AS20) used in this study; the surface tension coefficients are: d [-] = 0.0795, f [wt.-%] = 0.0164, and $g_{SOL,SAT}$ [N/m] = 33.3000×10^{-3} .

Placing Equation 4 into Equation 3, the Kelvin radius can be determined for drying samples at 0% and 5% concentration of SRA as shown in Figure 5(a). The reduction in surface tension reduces the pore size that is emptied at a given relative humidity. This implies that a specimen containing SRA should have a higher water loss, however it is estimated that the volume of water contained in these nano-pores is relatively small and a difference in weight would be difficult to determine. For example, this may only be 3-5% for specimens at 70% RH based on pore size distributions obtained from MIP measurements.

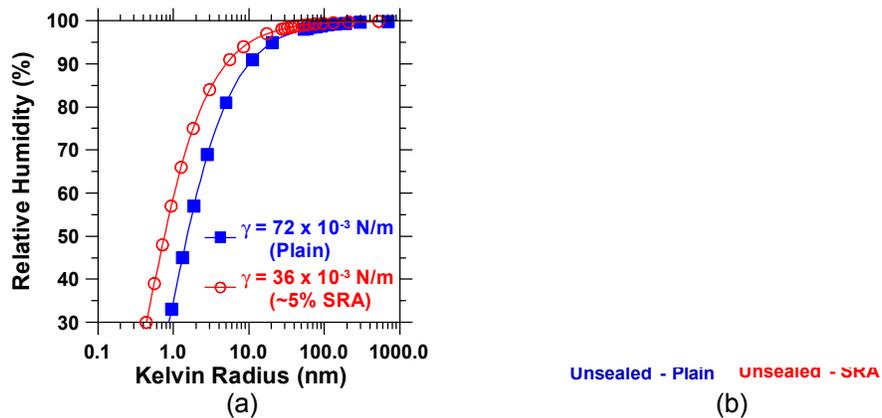


Figure 5: a) Moisture Loss from the Pore Structure of Sealed Samples as a Function of the Kelvin Radius using Equation 3 and b) Conceptual illustration of the reduction in internal relative humidity in sealed and drying samples for cement mixtures with and without SRA addition

It can now be argued that measurements of chemical shrinkage and non-evaporable water show that for the sealed specimens, the volume of water that is consumed by the hydration reaction is similar for both the plain and

SRA specimens (assuming that the influence of SRA on retardation is negligible) [12,26]. The implications of losing a constant volume of water (Figure 5(b), above) are that the specimen containing SRA maintains a higher internal RH, as illustrated using Figure 5(a). For example, if pores having a radius up to 5 nm are emptied, the plain mixture would have a relative humidity of 85% while the SRA mixture would display a relative humidity of 95%. This explains why SRA specimens in Figure 4 show a higher internal RH in sealed conditions at later ages. This assumes that the addition of SRA does not alter the pore structure of the system; however, conflicting reports exist in the literature as to the effects of a SRA on the pore structure of concretes [27]. Current research is investigating this effect further.

For the unsealed (i.e., drying) specimen, the volume of water that is lost is dictated by the external relative humidity. Using the Kelvin-Laplace-Young Equation (Equation 3), the relative humidity can be related to the radius of the pore that is emptied by drying as shown in Figure 5(a). It can be seen that a smaller pore radius is emptied in mixtures containing SRA than in plain mixtures for the same relative humidity. This would imply that while menisci are generally thought to describe the shrinkage response (i.e., loss of capillary water) in plain pastes from saturation to 45% relative humidity [28], in pastes containing SRA they would only describe the behavior down to approximately 70% relative humidity (from saturation) corresponding to a Kelvin radius of approximately 1.5 nanometers. This is as reflected in Figure 2(b) and Figure 3(b). As the capillary pores empty, the shrinkage reducing capillary stresses diminish. This is significant as such a response could explain the dramatic shrinkage reduction achieved with addition of SRA.

7. Conclusions

In conclusion, this paper has shown that shrinkage reducing admixtures (SRA's) can be used to reduce both the shrinkage of sealed specimens (autogenous shrinkage) and the shrinkage of unsealed specimens (exposed to external drying):

- In sealed specimens, the SRA causes a slight expansion, and maintains higher relative humidity, resulting in lower shrinkage.
- In drying specimens containing SRA, the SRA would be expected to empty pores to a smaller Kelvin radius (losing more water) at the same relative humidity. This would imply that the menisci in pastes containing SRA would describe the shrinkage response only at higher relative humidities (down to ~70% from saturation).

8. Acknowledgements

The authors gratefully acknowledge support for this research which has come from BASF Admixtures and the Center for Advanced Cement Based Materials. In addition, the authors would like to acknowledge the assistance of Guy Mazzotta in experimental testing and data acquisition.

9. References

- [1] Shoya, M., and Sugita M., 'Application of Special Admixture to Reduce Shrinkage Cracking of Air Dried Concrete', Hachinohe Institute of Technology, Hachinohe, Japan (1989) 1-11
- [2] Shah, S.P., Karaguler, M.E., and Sarigaphuti, M., 'Effects of shrinkage reducing admixture on restrained shrinkage cracking of concrete', *ACI Materials Journal* 89 (3) (1992) 88-90.
- [3] Weiss, W. J., Yang, W., and Shah, S. P., (1997). "Restrained Shrinkage Cracking in Concrete." 6th Int. Purdue Conference on Conc. Pavement: Design and Materials for High Perf., 159-175
- [4] Folliard, K.J. and Berke, N.S., 'Properties of high-performance concrete containing shrinkage reducing admixture', *Cem. and Conc. Res.* 27 (9) (1997) 1357-1364
- [5] Nmai, C., Tomita, R., Hondo, F., and Buffenbarger, J., 'Shrinkage reducing admixtures', *Concrete International* 20 (4) (1998) 31-37.
- [6] Shah, S.P., Weiss, W.J., and Yang, W., 'Shrinkage Cracking-Can it be prevented?', *Concrete International* 20 (4) (1998) 51-55
- [7] Ai, H., and Young, J.F., 'Mechanisms of shrinkage reduction using a chemical admixture', *Proc. of the 10th Int. Cong. on the Chemistry of Cement*, ed. Justnes, H., Gothenburg, Sweden, (1997) Vol. 3
- [8] Bentz, D., Geiker, M., and Hansen, K., 'Shrinkage-reducing admixtures and early age desiccation in cement pastes and mortars', *Cement and Concrete Research* 31 (7) (2001) 1075-1085.
- [9] Pease, B.J., 'The Role of Shrinkage Reducing Admixtures on Shrinkage, Stress Development, and Cracking', MSCE Thesis, Purdue University, West Lafayette, Indiana, May (2005) pp. 217.
- [10] Chapter 7.5 Weiss, W. J., and Berke, N.S., "Admixtures for Reduction of Shrinkage and Cracking", *Early Age Cracking In Cementitious Systems - State of the Art Rep.*, ed A. Bentur, 2002
- [11] Weiss, W. J., Yang, W. and Shah, S. P., 'Shrinkage cracking of restrained concrete slabs', *Journal of Eng. Mech. Div., ASCE* 124 (7) (1998) 765-774.
- [12] Sant, G., Rajabipour, F., Lura, P. and Weiss, J., 'Examining Time-Zero and Early Age Expansion in Pastes Containing Shrinkage

- Reducing Admixtures (SRA's)', 2nd RILEM Symp. on Advances in Conc. through Science and Eng., Quebec City, Canada (2006)
- [13] Schießl, A., Weiss, W.J., Shane, J. D., Berke, N. S., Mason, T.O. and Shah, S. P. 'Assessing the moisture profile of drying concrete using impedance spectroscopy', *Conc. Science and Eng.* 2 (2000) 106-116.
- [14] Weiss, W. J., Borischevsky, B. B., and Shah, S. P., (1999) "The Influence of a Shrinkage Reducing Admixture on the Early-Age Behavior of High Performance Concrete," 5th Int. Symp. on the Utilization of High Strength/HPC, Sandefjord, Norway, Vol. 2, 10
- [15] Fick, A., *Phil. Mag.* (1855), 10, 30
- [16] L'Hermite, R.G., *Volume Changes of Concrete*, 4th International Symp. on the Chem. of Cem., Washington D.C., 43, (1960)
- [17] Bazant, Z., 4th RILEM Int. Symp. on Creep and Shrinkage of Concrete Mathematical Modeling, *Materials and Structures*, 19, 6, 11/11/1986, Page 459
- [18] Weiss, W.J., 'Prediction of Early age Cracking in Thick Concrete Structures', PhD Thesis, Northwestern Univ., Evanston, IL, 1999.
- [19] Pickett, G., "Effect of Aggregate on Concrete Shrinkage and Hypothesis Concerning Shrinkage," *Jour. of ACI*, Vol. 52, (1956), 9
- [20] Bentz, D.P., Garboczi, E.J., and Quenard, D.A., 'Modelling drying shrinkage in reconstructed porous materials: application to porous Vycor glass', *Modelling Simul. Mater. Sci. Eng.* 6 (1998) 211-236.
- [21] MacKenzie, J.K., "The Elastic Constants of a Solid Containing Spherical Holes," *Proc. of the Physics Society*, V. 683, 1950, pp. 9
- [22] Sant, G., Lura, P. and Weiss, W.J., 'Measurement of Volume Change in Cementitious Materials at Early Ages: Review of Testing Protocols and Interpretation of Results', *Transportation Research Record* (2006) (in press)
- [23] Jensen, O.M. and Hansen, P.F., 'A dilatometer for measuring autogenous deformation in hardening Portland cement paste', *Mater. Struct.* 28 (181) (1995) 406-409
- [24] ASTM (2005), *Annual Book of ASTM Standards*, "Concrete and Aggregates", Vol. 4.02, © 2005
- [25] Shah, S. P., Weiss, W.J., and Yang, W., (1998). "Shrinkage Cracking-Can It Be Prevented?", *Concrete International*, Vol. 20, No. 4, 51-55 (Selected by Editors)
- [26] Sant, G., Rajabipour, F., Fishman, P., Lura P., and Weiss, J., 'Electrical conductivity measurements in cement paste at early ages', in: 'Int. Conf. on Adv. Testing of Fresh Cem. Materials', Stuttgart, Germany (2006)
- [27] Mora, I., Aguado, A. and Gettu, R., 'The influence of shrinkage reducing admixtures on plastic shrinkage', *Materiales de Construcción* 53 (271-72) (2003) 71-80.
- [28] Bazant, Z. P., "Mathematical Modeling of Creep and Shrinkage of Concrete," John Wiley & Sons, Inc., June 1989