

Influence of Shrinkage-Reducing Admixtures on Early-Age Properties of Cement Pastes

by

Dale P. Bentz
Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899 USA

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Influence of Shrinkage-Reducing Admixtures on Early-Age Properties of Cement Pastes

Dale P. Bentz¹

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Abstract

Because most shrinkage-reducing admixtures (SRAs) significantly reduce the surface tension of a cement paste pore solution, they will naturally influence all physical properties and processes that are dependent in some way on surface tension. Such properties include internal relative humidity, capillary stresses, and freezing point depression, all via the Kelvin equation and its variants (Kelvin-Laplace, Gibbs-Thomson). Processes that will thus be strongly influenced by the presence of SRAs include drying, autogenous stress and strain development, and freezing. In this paper, experimental measurements of these processes in cement pastes and mortars with and without SRA additions will be presented in light of the Kelvin equation. The experimental measurements that are applied to early-age specimens include X-ray absorption measurements to quantify drying profiles, bulk mass loss measurements, measurements of internal relative humidity, assessments of autogenous deformation under sealed curing conditions, and low temperature calorimetry scans to quantify freezable water content. The results indicate that SRAs can provide benefits in several new applications beyond their conventional usage to reduce drying shrinkage.

1. Introduction

In recent years, shrinkage-reducing admixtures (SRAs) have moved successfully from the research laboratory to being commercially viable admixtures that are often employed in field concrete to reduce drying shrinkage. Originally introduced in Japan in the 1980s (Sato *et al.* 1983), these materials became commonplace in the U.S. by the late 1990s (Folliard and Berke 1997, Nmai *et al.* 1998). While the specific chemical compositions of the SRAs vary amongst manufacturers, they generally reduce the surface tension of the pore solution (or of distilled water) by as much as 50 % or more, at typical recommended addition rates. It is worth noting that while SRAs will influence the surface tension and viscosity of the pore solution, these materials are usually dosed according to the mass of cement in the concrete mixture.

Because concrete is a porous material with a wide pore size distribution, this change in surface tension will have several effects that are described by the Kelvin-Laplace equation (and its variants such as the Gibbs-Thomson equation). For example, in a partially saturated concrete specimen, capillary stresses will be created within the remaining pore solution in (assumed) cylindrical-shaped pores, as described by Alberty and Daniels (1980):

$$\sigma_{cap} = \frac{2\gamma_{lg} \cos \alpha}{r} = \frac{-\ln(RH/100)RT}{V_m} \quad (1)$$

where

σ_{cap} : the capillary stress,

γ_{lg} : the surface tension of the pore solution,

α : the contact angle between pore solution and solids (often assumed to be 0°),

r : the radius of the largest (partially) water-filled pore,

RH : the internal relative humidity (RH) in percent,

R : the universal gas constant,

T : absolute temperature, and

V_m : the molar volume of the pore solution.

Attempts to measure the contact angles of various solutions on "cast" hydrated cement paste surfaces have yielded contact angle estimates of 28° and 7° for distilled water and a 10 % solution of SRA, respectively. This would suggest that the contact angle difference between an SRA solution and distilled water would partially mitigate the effects of the vastly reduced surface tension of the SRA solution relative to distilled water. According to equation (1), the internal RH, the pore radius of the largest water-filled pore, and the capillary stress in the pore solution can all potentially be influenced by a change in the surface tension of the pore solution depending on the imposed boundary conditions as determined by the specimen geometry and the environmental exposure conditions.

The surface tension of the pore solution may also influence the freezing point depression obtained in the porous concrete (Acker *et al.* 2001, Fagerlund 1973, Brun *et al.* 1977, Liu *et al.* 2003). For example, Acker *et al.* (2001) have derived the following expression for the equilibrium of ice with an aqueous solution in a capil-

¹Chemical Engineer, Materials and Construction Research Division, National Institute of Standards and Technology, Gaithersburg, USA.
E-mail: dale.bentz@nist.gov

lary:

$$\Delta T = \frac{2v_s \gamma_{ls} T_o \cos \alpha}{r \Delta H} + \frac{v_l \pi_l T_o}{\Delta H} \quad (2)$$

where

ΔT : the freezing point depression,

v_s and v_l : the specific volumes of ice and water, respectively,

γ_{ls} : the liquid-ice surface tension,

T_o : the freezing temperature of the bulk pore solution,

ΔH : the latent heat of fusion,

π_l : the osmotic pressure of the solution,

and the other terms are as previously defined above in equation (1). Conversely, Fagerlund (1973) presents the following expression (neglecting osmotic effects) that is based instead on the liquid-gas surface tension:

$$r = - \frac{2\gamma_{lg} M}{\rho_l \Delta H \ln \left(\frac{T_o - \Delta T}{T_o} \right)} \quad (3)$$

where

M : the molecular weight of the pore solution and

ρ_l : the density of the pore solution.

In the case of a steep thermal gradient, Brun *et al.* (1977) state that the freezing point depression should be proportional to the ratio γ_{lg}/γ_{ls} . While the general consensus is that equation (2) is the correct one, it should be kept in mind that Fagerlund based his initial selection of γ_{lg} over γ_{ls} on the fact that the former gave a better fit to the experimental data of Powers and Brownyard (1948). Although the liquid-gas surface tensions of water and

solutions containing an SRA are readily measured, measurement of the liquid-ice surface tension is much more difficult and to the author's knowledge, no such measurements for SRA solutions are to be found in the literature.

In this paper, a variety of experimental techniques will be applied to quantifying the properties and performance of cement pastes and mortars prepared with and without various SRA additions and the results will be interpreted in light of equations (1), (2), and (3).

2. Methods and materials

As many of the experimental details have been provided elsewhere (Bentz *et al.* 2001a, Bentz *et al.* 2002, Bentz 2005), they will only briefly be summarized here. Different cement pastes and mortar specimens were prepared and evaluated as detailed in Table 1. The following measurements were performed on the pastes and mortars: X-ray transmission (absorption) (Bentz *et al.* 2001a, Bentz and Hansen 2000), bulk mass loss, internal RH (Jensen and Hansen 1995a, Jensen and Hansen, 1996), autogenous deformation (Jensen and Hansen 1995b, Jensen and Hansen 1996), and low temperature calorimetry (LTC) (Bentz and Stutzman 2006). In addition, the viscosity of distilled water and 10 % solutions (by mass) of two different SRAs were measured using a Cannon-Fenske Routine Viscometer. SRAs from two different manufacturers were also used for the LTC experiments, while only one of the SRAs (SRA A) was used for the experiments to quantify water movement, mass loss, internal RH, and autogenous deformation. According to their respective MSDS, one of the SRAs is

Table 1 Cement pastes and mortars evaluated with and without SRA additions.

| Cement Type (reference) | Paste or mortar | Water-to-cementitious material ratio (w/cm) | SRA addition (by mass of cement) | Mixing Technique Employed | Measurements Performed |
|--|-----------------|---|-------------------------------------|---------------------------|---|
| Low alkali sulfate resistant (Bentz <i>et al.</i> 2001a) | Paste | 0.35 | 2 % SRA A | Hand mixing | X-ray absorption |
| Ultrafine (Bentz <i>et al.</i> 2001a) | Paste | 0.30 | 2 % SRA A | Hand mixing | Internal RH, degree of hydration |
| Low alkali with 8 % silica fume (Bentz <i>et al.</i> 2001a, Bentz <i>et al.</i> 2002) | Mortar | 0.35 | 2 % SRA A | Epicyclic (Hobart) mixer | Internal RH, autogenous shrinkage, strength |
| Cement and Concrete Reference Laboratory (CCRL) Cement 140 (Bentz 2005, Cement and Concrete Reference Laboratory 2001) | Mortar | 0.40 | Topical 10% and 20% solutions SRA A | Epicyclic mixer | Mass loss, degree of hydration |
| CCRL Cement 152 (Cement and Concrete Reference Laboratory 2004) | Paste | 0.35 | 1 % to 3 % SRAs A and B | High speed blender | LTC, degree of hydration |

based on a polyoxyalkylene alkyl ether, while the other is based on aliphatic propylene glycol ethers.

3. Results and discussion

In 5 mm to 10 mm thick specimens of fresh cement paste, it has previously been noted that drying occurs uniformly throughout the specimen thickness as opposed to proceeding as a "sharp" front from the surface exposed to the drying environment (Bentz and Hansen 2000). **Figure 1** exemplifies this observation, indicating the X-ray counts transmitted through a cement paste specimen with water-to-cement ratio, $w/c=0.35$, as a function of hydration/drying time when exposed to a 23 °C, 50 % RH environment. As the specimen dries during the first 96 h, the X-ray counts are seen to increase in a relatively uniform fashion throughout the 8 mm thickness of the specimen; greater counts indicate a less dense (less X-ray absorption) material and indicate the loss of water at each sampled depth within the specimen. Similar results have been observed for pastes with other w/c ratios (Bentz and Hansen 2000) and also for mortars (Bentz *et al.* 2001b). Surprisingly, as shown in **Fig. 2**, the addition of an SRA modifies this behavior such that during the first 6 h to 8 h of curing, a rather sharp drying front is observed at the top exposed surface of the specimen. It is hypothesized that initial drying of the specimen concentrates the SRA in the remaining pore solution at the top surface, such that it is no longer able to "pull" higher surface tension solution from deeper within the specimen to the top surface (Bentz *et al.* 2001a, Bentz 2005). This also results in a concurrent reduction in the rate of mass loss from specimens with an SRA addition relative to those with no SRA, when the SRA is added either to the initial bulk mixture (Bentz *et al.* 2001a, Lura *et al.* 2006) or as a topical solution applied as a curing aid (Bentz 2005). Interestingly, Lura *et al.* (2006) have shown that due to this reduction in drying rate and the accompanying reduction in the rate of increase of capillary stresses (equation 1) when an SRA is present, a significant reduction in plastic shrinkage cracking is also observed. The reduced drying rate will also result in a greater quantity of water remaining in the specimen, resulting in a higher achieved degree of hydration of the cement at later ages (Bentz 2005). Thus, SRAs may soon find a new field application in reducing evaporative water loss from specimens exposed to a drying environment at early ages and in reducing the often concurrent plastic shrinkage cracking.

While SRAs have been commonly employed to reduce drying shrinkage, according to equation (1), they also may have a significant influence on the autogenous deformation occurring in a cement-based material cured under sealed conditions (Bentz *et al.* 2001a, Rongbing and Jian, 2005). According to equation (1), if the same size pores (r) are being emptied in specimens with and without SRA additions, the lower surface tension in the specimen with the SRA should result in a reduction in

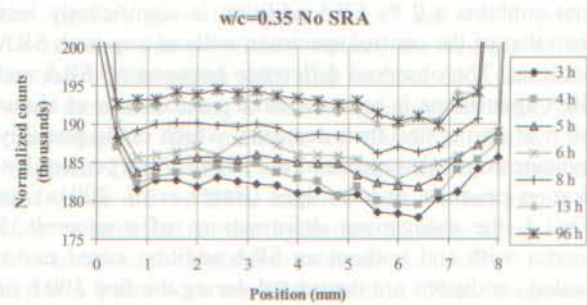


Fig. 1 Normalized counts for X-rays transmitted through a $w/c=0.35$ low alkali sulfate resistant cement paste specimen (10 mm by 10 mm by 7 mm deep) with no SRA addition, immediately exposed to drying conditions (23 °C and 50 % RH) at its top surface only, as a function of curing time (3 h to 96 h) and depth (Bentz *et al.* 2001a). Top of specimen is located at about 8 mm. Uncertainty in the normalized count values is on the order of 0.4 % (Bentz and Hansen 2000).

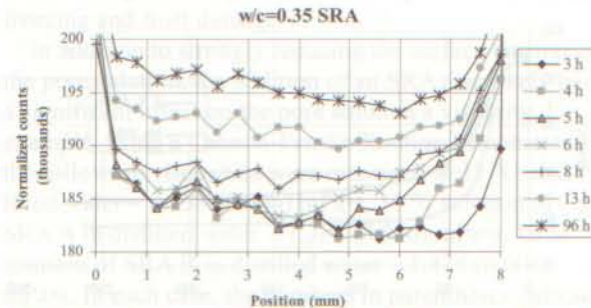


Fig. 2 Normalized counts for X-rays transmitted through a $w/c=0.35$ low alkali sulfate resistant portland cement paste specimen (10 mm by 10 mm by 7 mm deep) with a 2 % SRA addition by mass of cement, immediately exposed to drying conditions (23 °C and 50 % RH) at its top surface only, as a function of curing time (3 h to 96 h) and depth (Bentz *et al.* 2001a). Top of specimen is located at about 8 mm. Uncertainty in the normalized count values is on the order of 0.4 % (Bentz and Hansen 2000).

the capillary stress (σ_{cap}) and in the maintenance of a higher internal RH within the specimen. A reduction in capillary stress should directly translate into a concurrent reduction in the measured autogenous deformation (Bentz 2005).

Both internal RH and autogenous deformation have been monitored in pastes and mortars with and without SRAs and example results are presented in **Fig. 3** and **4**. For **Fig. 3**, a low $w/c=0.3$ cement paste was prepared using an ultrafine cement (Blaine fineness of 654 m^2/kg) in order to maximize the reduction in internal RH that would occur during the first several hundred hours of curing. As would be expected from equation (1), the observed reduction in the internal RH for the specimen

that contains a 2 % SRA addition is significantly less than that of the control specimen without any such SRA addition. The observed difference between no SRA and SRA specimens is seen to reach a maximum at about 50 h of curing and then decrease, which could possibly indicate some absorption of the SRA by the cement hydration products at later ages (Bentz *et al.* 2001a). In Fig. 4, the autogenous deformations of a $w/cm=0.35$ mortar with and without an SRA addition cured under sealed conditions are contrasted during the first 500 h of curing. From equation (1), it would be expected that the mortar with the SRA addition would develop lower capillary stresses within the pore solution during the chemical shrinkage and self-desiccation that accompanies the cement hydration under sealed conditions. This is supported by the measured reduction in autogenous shrinkage by about a factor of 3 relative to the control specimen with no SRA addition. The results in Fig. 3 and 4 clearly indicate a second potential application for SRAs beyond their usage to reduce drying shrinkage, namely a

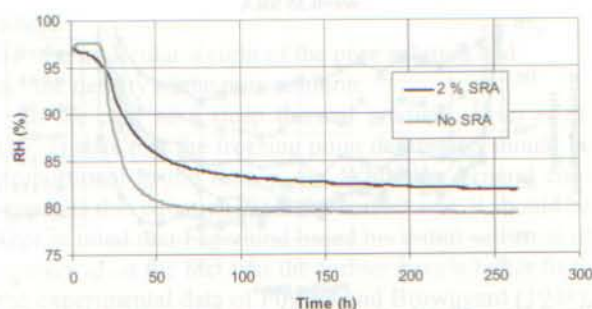


Fig. 3 Differences in internal RH (Jensen and Hansen 1995a) for ultrafine cement pastes ($w/c=0.3$) with and without SRA, cured under sealed conditions at 25 °C (Bentz *et al.* 2001a). For replicate specimens, the maximum standard deviation in RH was 0.42 %, with an average standard deviation of 0.17 % (Bentz *et al.* 2001a).

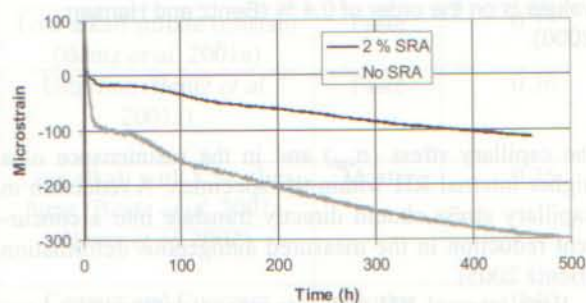


Fig. 4 Differences in autogenous deformation (Jensen and Hansen 1996) for cement mortars ($w/cm=0.35$) with and without SRA, cured under sealed conditions at 30 °C (Bentz *et al.* 2001a). For replicate specimens, the maximum standard deviation in deformation was 27 microstrains, with typical standard deviations being in the range of 5 microstrains to 17 microstrains (Bentz *et al.* 2001a).

significant reduction in autogenous shrinkage and the possible avoidance of early-age cracking that often accompanies such deformation.

Equations (2) and (3) indicate that an SRA addition could also potentially influence the observed freezing point depression in the small pores within a hydrating cement paste microstructure. To examine this possibility, LTC scans have been conducted with a scan rate of -0.5 °C/min from 5 °C to -55 °C (Bentz and Stutzman 2006). For an ordinary portland cement paste with no SRA addition, as many as three peaks are typically observed in an LTC scan: a peak near -15 °C corresponding to water freezing in percolated capillary pores, a second peak near -25 °C corresponding to water freezing in open gel pores (and capillary pores surrounded by open gel pores), and a third peak between -40 °C and -45 °C corresponding to water freezing in pores with dense gel pore entryways (Snyder and Bentz 2004). For lower w/c cement pastes (e.g., ≤ 0.45), the former two peaks will disappear at later ages corresponding to the depercolation of first the capillary pores and then the open gel pores (Bentz and Stutzman 2006, Snyder and Bentz 2004). Such behavior can be observed in Fig. 5 to 7 for the $w/c=0.35$ cement paste with no SRA addition. At 3 d (Fig. 5), all three peaks are present, although the percolated capillary pore peak is already becoming quite small. By 5 d (Fig. 6), the percolated capillary pore peak is no longer present for the control (no SRA) specimen and by 7 d (Fig. 7) the percolated open gel pore peak is also becoming quite small.

As illustrated in Fig. 5 to 7, for the cement pastes with a 1 % or 3 % addition of the two different SRAs, a quite different set of LTC scans are obtained. At 3 d, for the three pastes with SRA additions in Fig. 5, only a single (large) peak near -15 °C is observed. As shown in Figs. 6 and 7, at ages of 5 d and 7 d, small peaks near -25 °C and -45 °C do begin to appear (more so for the pastes with the 1 % additions), but a much larger peak near -15 °C remains. Based on equation (3), a reduction in surface tension on the order of 50 % due to the addition of an SRA would shift freezing point depressions of -45 °C and -25 °C to values of -19 °C and -12 °C, respectively. Thus, these peaks would be occurring in the

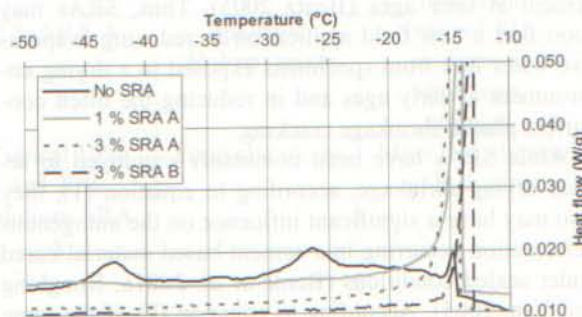


Fig. 5 LTC scans for a $w/c=0.35$ ordinary portland cement paste with various SRA additions by mass of cement, cured under saturated conditions at 20 °C for 3 d.

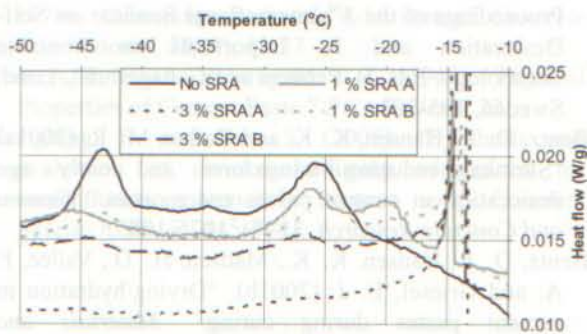


Fig. 6 LTC scans for a $w/c=0.35$ ordinary portland cement paste with various SRA additions by mass of cement, cured under saturated conditions at $20\text{ }^{\circ}\text{C}$ for 5 d.

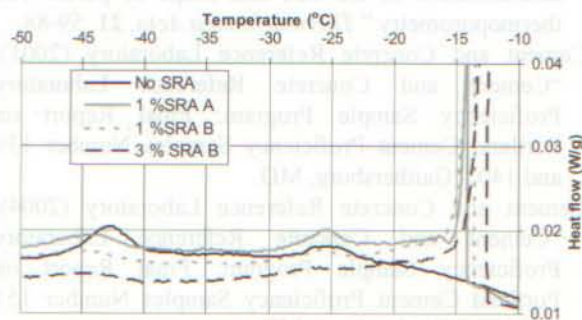


Fig. 7 LTC scans for a $w/c=0.35$ ordinary portland cement paste with various SRA additions by mass of cement, cured under saturated conditions at $20\text{ }^{\circ}\text{C}$ for 7 d.

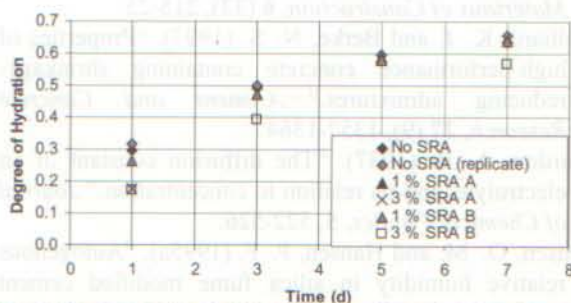


Fig. 8 Degree of hydration as a function of curing time for a $w/c=0.35$ ordinary portland cement paste with various SRA additions by mass of cement, cured under saturated conditions at $20\text{ }^{\circ}\text{C}$. The expanded uncertainty ($k=2$) in the measured degree of hydration is 0.004 (Bentz and Stutzman 2006).

same temperature range near $-15\text{ }^{\circ}\text{C}$ where freezing in the percolated capillary pores is observed. This hypothesis appears to be quite consistent with the observed results in Figs. 5 to 7. Of course, in addition to their influence on the pore solution surface tension, the SRAs could also influence the developing pore structure of the hydrating cement paste. For example, by retarding the hydration, an SRA would be expected to produce LTC scans that would exhibit a later depercolation of

the capillary pores (disappearance of the $-15\text{ }^{\circ}\text{C}$ peak). To examine this possibility further, the degrees of hydration of the pastes with and without SRA additions were measured using a loss-on-ignition technique, and correcting for the presence of the SRA (Bentz and Stutzman 2006). The results provided in Fig. 8 indicate that while a 3 % SRA addition does indeed result in some retardation in the hydration at early ages, for a 1 % addition, the hydration rates are nominally the same as for a paste with no SRA addition. Thus, it appears that the most likely explanation for the observed differences in the LTC scans for pastes without and with SRA additions is that the freezing point depressions are significantly reduced in the latter case due to the reduced liquid-gas (measured) and/or liquid-ice (hypothesized only) surface tensions of the pore solution. The practical implication of this, as clearly indicated in Fig. 5 to 7, is that there is a significantly greater quantity of (readily) freezable water in the specimens with the SRA additions. Field concrete specimens containing an SRA could thus potentially be more susceptible to early-age freezing and frost damage.

In addition to strongly reducing the surface tension of the pore solution, the addition of an SRA also likely has a significant effect on the pore solution's viscosity. For example, using a Cannon-Fenske Routine Viscometer, the following viscosities were measured at $22\text{ }^{\circ}\text{C}$: distilled water – 0.958 (0.006) mPa·s, 10 % solution of SRA A in distilled water – 1.388 (0.006) mPa·s, 10 % solution of SRA B in distilled water – 1.478 (0.004) mPa·s. In each case, the numbers in parentheses indicate the standard deviation obtained from either four or five replicate measurements of the same solution. The value measured for distilled water is in excellent agreement with that provided in the literature (CRC Handbook 1987). For both SRAs, the viscosity of a 10 % solution in distilled water is 45 % to 55 % greater than that of distilled water itself. Because diffusion coefficients should be inversely proportional to the viscosity of the pore solution (Gordon 1937), one might expect that the diffusion coefficients in concretes prepared with SRAs could be favorably reduced by a factor of about 1.5 relative to those in concrete prepared without any SRA additions. This expectation must be contrasted against the experimental observation of Folliard and Berke (1997), who noted “no significant effect of SRA addition on the rapid chloride permeability of concrete.” However, because the rapid chloride permeability test actually assesses electrical conduction and not ionic diffusion, it may be insensitive to the change in viscosity and its effect on the inherent diffusivity (physical movement) of ions in the bulk pore solution. A second possibility could be that the viscosity effect of the SRA addition is perhaps offset by concurrent changes to the pore structure (less hydration or coarser and more percolated pores) of the hydrating cement paste in the presence of an SRA.

4. Conclusion

The influences of shrinkage-reducing admixtures on a variety of processes in cement-based materials have been examined within the framework of their primary influence on the surface tension of the cement paste pore solution. In addition to their well known influence on drying shrinkage, SRAs also affect drying profiles and drying rates of fresh cement-based materials, internal RH and autogenous deformation at early ages, freezing point depressions within the porous networks, and the viscosity of the pore solution (and potentially diffusion). SRAs may be used beneficially to reduce evaporative water loss from fresh concrete, to reduce autogenous shrinkage, and thus to reduce early-age cracking whether due to plastic shrinkage or autogenous deformation. The significantly greater quantity of freezable water (at around -15°C) in specimens prepared with an SRA will require that appropriate attention be paid to the placement and curing of SRA-containing concretes in cold climate conditions. Finally, in addition to reducing the surface tension of the pore solution, the addition of an SRA should also significantly increase the pore solution viscosity, which could potentially have beneficial implications for reducing the diffusion coefficients of deleterious ions (chloride, sulfate, etc.) in cement-based materials.

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