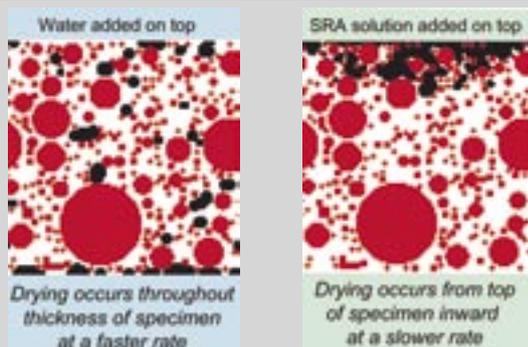


Curing with Shrinkage-Reducing Admixtures

Beyond drying shrinkage reduction

BY DALE P. BENTZ



Two-dimensional microstructure images from three-dimensional computer simulations.⁷ Red indicates the solid cement particles, white the water-filled pores, and black the empty (dry) pores.

In a water-treated specimen (left), the small capillaries in the mortar wick water to the surface, where it evaporates. The wicking action draws water from the larger pores below that act as reservoirs. However, with SRA treatment (right), even the smallest capillaries are emptied at the surface. There is therefore no continuous path for water to wick to the surface, leaving more water available for curing. While the application of an SRA solution does not eliminate evaporative water loss, the overall loss is reduced sufficiently to warrant investigation of SRAs as new tools for curing.

Shrinkage of concrete, along with the cracking that often accompanies it, has been a continual concern of the concrete construction community.^{1,2} In the past 20 years or so, numerous shrinkage-reducing admixtures (SRAs) have been developed with the goal of reducing drying shrinkage and delaying or preventing cracking.²⁻⁶ Most SRAs function by reducing the surface tension of the pore solution in the concrete. In addition to reducing or slowing drying shrinkage, this reduction in surface tension can also potentially reduce autogenous shrinkage in mortars and concretes with low water-binder ratios as well as reduce evaporative water loss during early-age curing.^{6,7} In this article, a consistent theoretical basis for these reductions is presented along with example results illustrating the use of SRAs as potential curing compounds.

THEORY

A large part of concrete shrinkage during drying (external or internal) is controlled by capillary pressure developing in the partially water-filled pores, as illustrated schematically in Fig. 1. For a cylindrical pore that is partially filled with pore solution, the Kelvin equation⁸ describes the relationship between the pore radius and the relative humidity above the meniscus assuming complete wetting of the pore walls by the liquid:

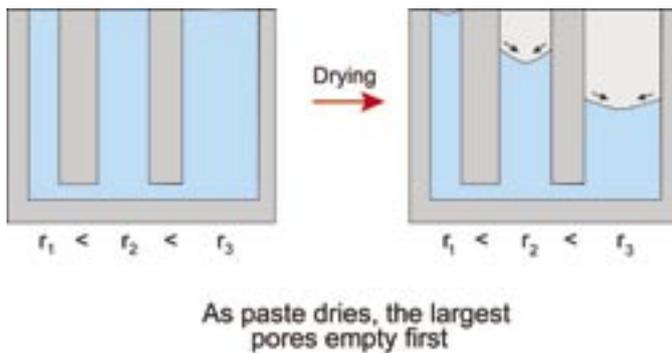


Fig. 1: As cement paste dries, water menisci create capillary stresses that cause shrinkage of the paste and possible cracking at restraints

$$\ln\left(\frac{\text{R.H.}}{100\%}\right) = \frac{-2\gamma V_m}{rRT} \quad (1)$$

where R.H. is the relative humidity (%), γ is the surface tension of the pore solution (N/m), V_m is the molar volume of the pore solution (m^3/mol), r is the pore radius (m), R is the universal gas constant [$8.314 \text{ J}/(\text{mol}\cdot\text{K})$], and T is absolute temperature (Kelvin). According to Eq. (1), as smaller and smaller pores are emptied in the concrete, whether due to self-desiccation or to external drying, the internal R.H. will decrease. There will also be a capillary tension created within the pore liquid given by:

$$\sigma_{cap} = \frac{2\gamma}{r} = \frac{-\ln(\text{R.H.}/100\%)RT}{V_m} \quad (2)$$

where σ_{cap} is the capillary stress (Pa). As an example using Eq. (1) and (2), when emptying pores with a radius of 50 nm (2×10^{-6} in.), the internal R.H. will decrease to about 98% (neglecting any further depression due to the alkalis in the pore solution) and a capillary stress on the order of 3 MPa (440 psi) will be generated. These capillary stresses will cause deformation of the porous concrete or mortar. This can be approximated using a slight modification⁹ of MacKenzie's equation:¹⁰

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

where ε is the linear strain or shrinkage, S is the saturation or fraction of water-filled pores (with values between 0 and 1), and K and K_s are the bulk moduli (Pa) of the porous material with empty pores (dry) and the solid framework within the porous material, respectively. This equation is strictly valid for a fully saturated linear elastic material and is only an approximation for partial saturation and for viscoelastic cement-based materials. It should be further noted that both S and σ_{cap} will be strong functions of the pore size distribution of the hardening cement-based material. A material with finer pores will either maintain a higher saturation at a given equilibrium

R.H. or produce much larger capillary stresses at a given fixed saturation. In either case, for fixed values of the bulk and solid framework moduli (K and K_s in Eq. (3)), the material with finer pores would exhibit higher shrinkage.

Looking carefully at Eq. (1) to (3) leads to an interesting hypothesis concerning drying shrinkage and SRAs. In a normal drying shrinkage exposure (in the laboratory), the external R.H. is typically fixed at some value below 100%, and the resulting shrinkage over time is monitored as the specimens' internal R.H. slowly approaches the external value. Equation (2) indicates that for a given fixed relative humidity and temperature exposure, the equilibrium capillary stress in the pore solution will be the same and would not be a function of the surface tension of the pore solution. However, for such a fixed R.H. (and fixed capillary stress level), a lower surface tension will reduce the size of the pores (the r term in Eq. (2)) that are emptied under drying once (and if) equilibrium is finally achieved. If smaller pores are emptied in the presence of an SRA, the bulk equilibrium mass loss of the specimens containing the SRA should be greater than specimens with no SRA, as has indeed been observed for cement paste specimens.³ As a consequence of this, in Eq. (3), the incorporation of an SRA would actually influence S and not σ_{cap} , which would itself simply be proportional to $-\ln(\text{R.H.}/100\%)$, regardless of the presence or absence of the SRA.

Because mass loss is often not measured during a drying shrinkage experiment (and equilibrium mass loss may not even be achieved during the length of a typical experiment),¹¹ there is only a limited amount of data available to evaluate this hypothesis. However, one of the earliest data sets (Sato, Goto, and Sakai³) does provide both mass loss and shrinkage measurements for cement paste specimens (prepared with four different levels of SRA addition) exposed to 12 different R.H. levels. In that study, 8 weeks were allowed for the cement paste specimens to come to equilibrium with the various external R.H. conditions.³ According to Eq. (3), shrinkage should be linearly related to the product of saturation and capillary stress. From Eq. (2), capillary stress will, in turn, be directly proportional to $-\ln(\text{R.H.}/100\%)$.

Analyzing the data of Sato, Goto, and Sakai³ based on Eq. (3) produces the plot shown in Fig. 2. A basically linear relationship exists between measured shrinkage values and a computed factor that should be directly proportional to the stress level. For this analysis, the equilibrium saturation S for each specimen at each R.H. was assumed to be proportional to the estimated water content remaining in the specimens after 8 weeks. Based on their measurements, the maximum mass loss after 8 weeks at 0% R.H. (the evaporable water) was used to estimate a water content for the specimens at complete saturation (equal to 325 mg/mL paste). Thus, the quantity

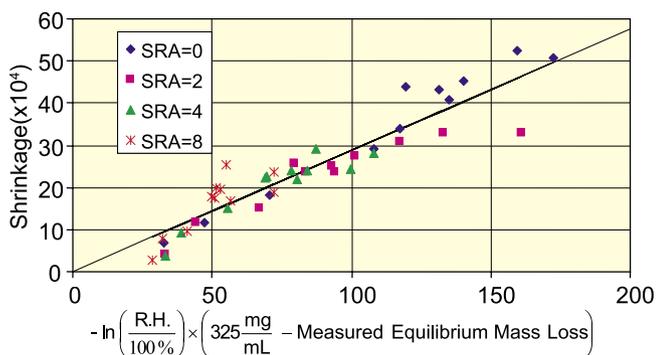


Fig. 2: Shrinkage of pastes with SRA contents³ of 0, 2, 4, and 8% versus proposed form of shrinkage stress (proportional to the first two terms on the right-hand side of Eq. (3)). Solid line indicates best-fit to experimental data that passes through the origin ($R^2 = 0.87$)

(325 mg/mL—the measured equilibrium mass loss) represents S for each individual specimen.

In addition to considering the equilibrium drying shrinkage based on Eq. (1) to (3), the kinetics of water evaporation (drying) and the resultant shrinkage must be considered.¹¹ Generally, mortars and cement pastes with SRA additions exhibit slower drying, resulting in less mass loss at equal drying times than the corresponding material without SRA addition.^{6,7} Thus, looking at Eq. (3), at equal times, S will often be greater in the specimens with the SRA. Still, their measured shrinkage could be less, as σ_{cap} would be expected to be significantly reduced for two reasons: 1) γ is reduced because of the SRA, and 2) r (for the largest partially water-filled pores) is increased because of the higher S . However, this implies that equilibrium has not yet been reached in the drying specimens and that their current internal R.H. is far from what would be the final equilibrium value. Depending on the drying conditions, specimen geometry, and mixture proportions, equilibrium may actually take several years to achieve.¹¹

While self-desiccation involves different moisture transport boundary conditions than drying, Eq. (1) to (3) can still be used to examine the influence of surface tension reduction on resultant autogenous deformation.¹² In this case, it is not the equilibrium R.H. that is fixed, but rather the volume of empty pores created during self-desiccation. For materials with a similar pore size distribution, one would expect this to correspond to a fixed value of r in Eq. (1) and (2), and a fixed value of S in Eq. (3). Thus, in the presence of an SRA, the reduction in γ will result in a direct reduction in the capillary stress and an increase in the equilibrium internal R.H. Direct measurements of the internal R.H. of both cement pastes and mortars cured under sealed conditions with and without the addition of an SRA have indeed indicated that less R.H. reduction occurs when an SRA is present in the mixture.⁷ Mixtures with an SRA have also exhibited

TABLE 1: INFLUENCES OF A REDUCTION IN SURFACE TENSION ON DRYING PHENOMENA IN CONCRETE CAUSED BY THE ADDITION OF SRA

Phenomena	Influence of Surface Tension Reduction
Drying shrinkage	Reduction in equilibrium saturation Reduction in drying rate (less mass loss)
Autogenous shrinkage	Reduction in capillary stresses Reduction in internal relative humidity
Early-age evaporation	Change in shape of drying profile Reduction in drying rate

substantially less autogenous shrinkage during sealed curing,^{6,7} as would be expected from consideration of Eq. (1) to (3).

One other influence of shrinkage-reducing admixtures on early-age properties is that in addition to altering the drying kinetics, they also change the shape of the drying profile within fresh cement pastes and mortars.⁷ Normally, the top 10 to 20 mm (3/8 to 3/4 in.) of an exposed fresh paste or mortar is observed to dry out fairly uniformly throughout its thickness, as the largest pores everywhere are emptied first, regardless of their depth within the specimen.¹³ However, with the incorporation of an SRA into the pore solution, a fairly sharp drying front forms at the specimen's exposed surface.⁷ This can result in a dramatic difference in the water distribution in the specimens with and without an SRA. As the SRA becomes concentrated in the pore solution remaining at the top surface during the initial drying, the surface tension of the local solution is further decreased such that it can no longer easily pull pore solution upward from deeper within the specimen. The specimen will thus enter a stage of drying by capillary action, with a concurrent decrease in its drying rate relative to that achieved during evaporative drying.¹⁴ As mentioned previously, this results in the drying rates of a fresh cement paste or mortar being significantly reduced by the addition of an SRA, even though the evaporation rate of the pore solution is (as with bulk solutions) accelerated by the reduction in surface tension caused by SRA addition.⁷ The influences of a reduction in surface tension of the pore solution on drying shrinkage, autogenous shrinkage, and early-age evaporative water loss are summarized in Table 1.

The observation that the shape of the drying profile changes when the surface tension of the pore solution is reduced suggests that it might be possible to develop a curing method based on the application of a solution containing an SRA to the exposed surface of mortar or concrete specimens. Previously, Nmai et al.⁵ presented the topical application of an SRA as an effective method for reducing 28-day drying shrinkage of concretes with water-cement ratios (w/c) of 0.45 and 0.65, thicknesses of

TABLE 2:
MIXTURE PROPORTIONS FOR MORTAR USED IN STUDY

Material	Mass
CCRL Cement 140	1875 g (4.13 lb)
Water	750 g (1.65 lb)
F95 fine sand	891 g (1.96 lb)
Graded (ASTM C 778 ¹⁷) sand	677 g (1.49 lb)
20-30 (ASTM C 778 ¹⁷) sand	677 g (1.49 lb)
S16 coarse sand	1318 g (2.90 lb)

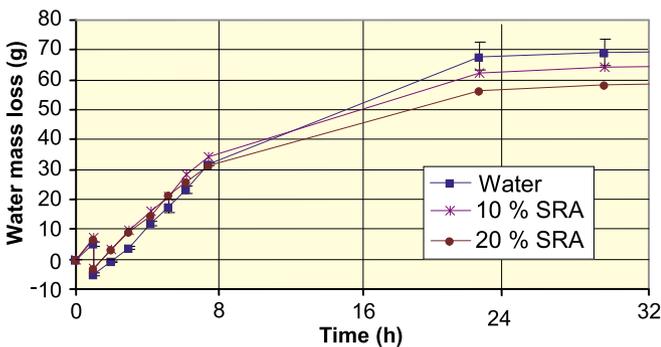


Fig. 3: Evaporative water loss versus time when the additional liquids are applied 1 hour after casting. Two samples were evaluated for each of the three different solutions. Error bars for water results indicate \pm one standard deviation ($1 \text{ g} = 0.0353 \text{ oz}$)

50 and 100 mm (2 and 4 in.), and application rates of 200 and 300 mL/m² (0.63 and 0.94 fl oz/ft²). In the current study, as a first step in investigating this possibility, the evaporative water loss and achieved degree of hydration of mortar specimens treated with two different concentrations of SRA solution are compared to those treated with only distilled water. Reduced (diluted with water) dosages on the order of 50 to 100 mL/m² (0.16 to 0.31 fl oz/ft²) were employed. Also, the initial evaporation rates and achieved hydration were evaluated, as opposed to the drying shrinkage. It should be noted that this approach of applying an SRA solution is different from that of applying a conventional evaporation reducer that forms a film on the surface of the mortar or concrete to reduce evaporation.¹⁵

TESTING

Cement mortars with a *w/c* of 0.40 were prepared using Cement and Concrete Reference Laboratory (CCRL) proficiency cement sample 140¹⁶ and a blend of four sands. Complete mixture proportions are provided in Table 2. The mortars were prepared in accordance with ASTM C 305-99¹⁸ and immediately cast into 127 x 178 mm (5 x 7 in.) plastic photographic trays to a depth of about 16 mm (5/8 in.). About 920 g (2 lb) of mortar were placed in each tray.

The trays were weighed and immediately placed in an environmental chamber maintained at 23 °C (73 °F) and 50% R.H. One, 2, or 3 hours after mixing, the mortars were

weighed once again and then sprayed with distilled water or an SRA solution. The solution was a mixture of distilled water and 10% or 20% by weight of a commercially available SRA. The amount of liquid applied was typically 10 g (0.35 oz). To monitor the subsequent evaporative water loss, the trays were weighed immediately after applying the liquid and periodically over the course of the subsequent drying exposure.

At the conclusion of the drying exposure, degrees of hydration were estimated using loss-on-ignition (LOI) analysis, correcting for the LOIs of the cement powder and the four sands used in the mortar mixtures. Based on a propagation of error analysis, the estimated uncertainty in the calculated degree of hydration was 0.01.¹⁹

In a separate casting, three small cuvettes (square glass test tubes), 10 x 10 x 40 mm (0.4 x 0.4 x 1.6 in.), were filled with the mortar and about 0.2 g (0.007 oz) of the curing solutions were immediately added to the top of each cuvette. After curing for 6 days at 23 °C (73 °F) and 55% R.H., the specimens were removed from each cuvette, broken in half, and the evaporable and non-evaporable water contents of the top and bottom sections of each specimen were determined by heating in an oven at 105 °C (221 °F) overnight, followed by heating in a furnace at 1000 °C (1830 °F) for 4 hours.

RESULTS AND DISCUSSION

The measured evaporative water losses versus time are provided in Fig. 3, 4, and 5 for the 1-, 2-, and 3-hour applications, respectively. Both the timing of the solution addition and the SRA concentration had significant influences on the subsequent evaporative water loss. These results are consistent with the previous observation that SRA addition accelerates evaporation from bulk solutions, but retards evaporation from cement pastes and mortars.⁷

Application at 1 hour

Following the 1-hour application, a layer of the sprayed-on solution remained on the top surface of the specimens. Specimens sprayed with the solutions that contained SRAs initially lost mass at a faster rate than the specimens sprayed with only distilled water (Fig. 3). For example, 2 hours after the application of the curing solutions, the specimens sprayed with water lost only 8.6 g (0.30 oz) of their mass (relative to their 1-hour value), while those sprayed with 10% and 20% SRA solutions lost 12.9 and 12.3 g (0.46 and 0.43 oz), respectively. However, as the layer of solution receded into the porous mortar microstructure, the subsequent rate of mass loss was diminished in the specimens sprayed with the SRA solutions. After 24 hours, the overall mass loss was greatest in the specimens sprayed with water. The total water losses for the three types of specimens after 24 hours (including the 10 g of added solution) were

about 79, 73, and 67 g (2.8, 2.6, and 2.4 oz), for the water, 10% SRA, and 20% SRA solutions, respectively.

Application at 2 hours

After the initial 2 hours of curing, the specimens had all lost about 10 g (0.35 oz), resulting in visually dry top surfaces. The sprayed-on solutions immediately penetrated into the top layer of the porous mortar. The subsequent drying kinetics for specimens treated with SRAs were characteristic of those of a saturated porous material (and not of a bulk solution). From the time of application forward, the specimens with the SRA had a lower mass loss (Fig. 4). After 24 hours, the cumulative losses were about 76, 67, and 60 g (2.7, 2.4, and 2.1 oz), for the water, 10% SRA, and 20% SRA solutions, respectively. Compared to the 1-hour application, the 2-hour application resulted in less cumulative mass loss after a 24-hour exposure, and the benefits are more clearly seen (Fig. 4 compared to Fig. 3).

Application at 3 hours

For the 3-hour application (Fig. 5), the influence of the SRA on the drying kinetics was once again characteristic of that in a saturated porous material, rather than a bulk solution. However, because of the higher mass loss prior to the application of the curing solutions, the 3-hour application was inferior to the 2-hour application in terms of overall 24-hour mass loss. Thus, for these particular drying conditions, sample geometries, and addition rates, a 2-hour delay before applying the liquid solutions by spraying appears to be optimum.

These results demonstrate that the timing of the “curing solution” application will be critical to its successful performance. Too early of an application will result in a more rapid evaporation of the solution on the top surface and would also likely lead to additional runoff under actual field conditions. It appears that the optimum time to apply the curing solution is when the top surface of the concrete first appears dry and free of surface water, much the same as the current criteria for the application of curing compounds. The exact time when this condition occurs will naturally depend on the concrete mixture proportions and the environmental exposure conditions in the field.

Degrees of hydration and water contents

After curing for 6 days, the degrees of hydration of the mixtures treated 2 hours after casting with water, 10%, and 20% SRA solutions were 0.25, 0.32, and 0.32, respectively. Thus, treatment with the SRA solutions resulted in over a 25% increase in the degree of hydration under these rather severe curing conditions. After curing for 14 days, the degrees of hydration for mixtures treated 3 hours after casting with 10% and 20% SRA solutions were

22% and 33% higher, respectively, than those treated with water only. These increases were 18% and 41% for the mixtures treated 1 hour after casting and cured for 28 days (6 days at 23 °C [73 °F] and 50 % R.H. followed by 22 days sealed in a plastic bag at 23 °C [73 °F]).

The increase in both evaporable and non-evaporable water contents for the smaller cuvette specimens is

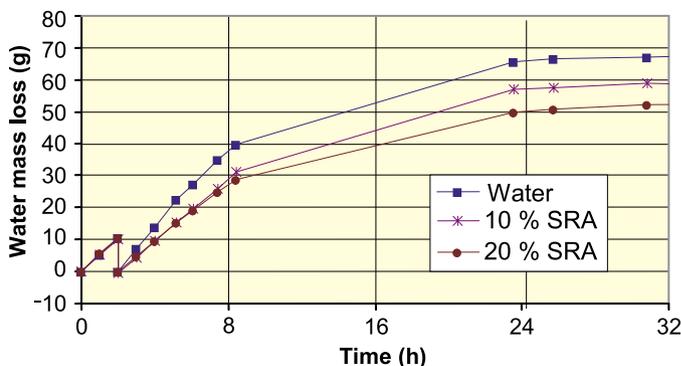


Fig. 4: Evaporative water loss versus time when the additional liquids are applied 2 hours after casting. One sample was evaluated for each of the three different solutions (1 g = 0.0353 oz)

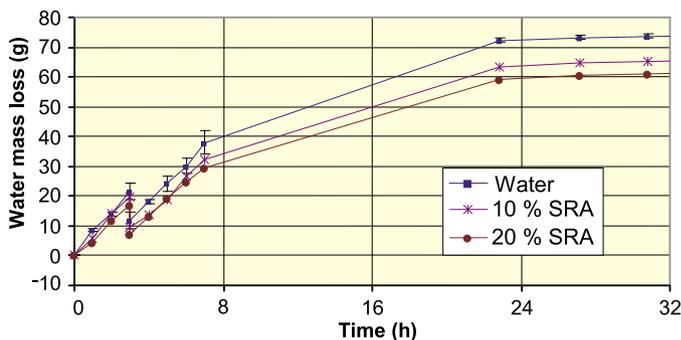


Fig. 5: Evaporative water loss versus time when the additional liquids are applied 3 hours after casting. Error bars for water results indicate ± one standard deviation between three samples (1 g = 0.0353 oz)

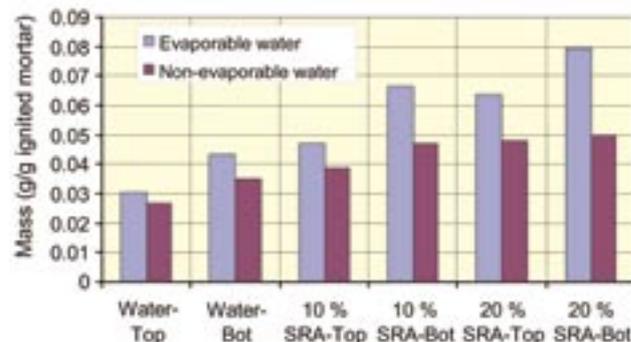


Fig. 6: Water contents of small cuvette specimens after exposure for 6 days to 23 °C (73 °F), 50% R.H. environment following immediate (after casting) application of the “curing” solutions. The labels of the x-axis indicate first the applied solution and then whether the water contents were measured on the top (exposed) or bottom half (Bot) of the broken cuvette specimens

shown in Fig. 6. The application of a solution containing SRA to the tops of these specimens clearly results in an increased free water content and an increased amount of hydration (as indicated by the non-evaporable water content) in both the top and bottom portions of the specimens. After curing for 6 days, the cumulative mass losses of the specimens were 6.3%, 3.7%, and 2.0% of the initial as-cast masses, for the water, 10% SRA, and 20% SRA solutions, respectively.

BEYOND CONVENTIONAL USAGE

Potential applications of shrinkage-reducing admixtures beyond their conventional usage to reduce or slow drying shrinkage have been presented. In the case of autogenous deformation of specimens cured under sealed conditions, at a fixed amount (volume) of self-desiccation, the SRAs reduce the internal capillary stresses and thus the accompanying internal R.H. reduction and autogenous shrinkage. In the case of reducing evaporative water loss, application of a curing solution that contains an SRA modifies the shape of the drying profile created within the porous mortar or concrete, leading to a concurrent reduction in evaporation rates and an increase in achieved degree of hydration. While the evaporative water loss is by no means eliminated, the application of a SRA solution as opposed to only water can provide extra assurance that the concrete will remain more saturated internally and that the cement will hydrate to a greater extent.

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