

New Developments in Shrinkage Reducing Admixtures

(Partly extracted from "Influence of Shrinkage-Reducing Admixtures on Early-Age Properties of Cement Pastes" by Dale P. Bentz, Journal of Advanced Concrete Technology Vol.4, No.3, 423-429, October 2006 and "Admixtures: The niche generation" by Don Talend, A Publication # J960742 of The Aberdeen Group, Boston, MA 02210)

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. 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. The SRAs is based on polyoxyalkylene alkyl ether or aliphatic propylene glycol ethers.

Shrinkage-reducing admixtures (SRAs) provide a method to reduce the associated strains caused by drying and the resulting stresses. 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 are shown in Figure 1.

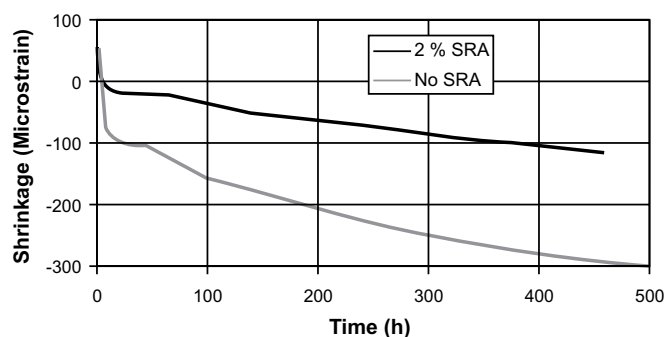


Figure 1: Autogenous deformation for cement mortars with and without SRA Advantages to this method are that with the exception of the added SRA, concrete mixture proportions and mixing requirements remain relatively unchanged. Thus, the drying shrinkage can be reduced for essentially any currently used concrete. Also increase moist curing reduces long-term drying shrinkage, concrete with SRA exhibits reduced drying shrinkage even if the moist curing is shortened. Random cracking caused by drying shrinkage is always undesirable, but it's particularly objectionable in bridge decks and parking garage slabs, where the cracks make rebar corrosion more likely. Cracking must also be controlled in secondary containment structures and vaults for hazardous material storage. Particularly, a polypropylene

glycol based Shrinkage-reducing admixture (SRA) helps in arresting such types of cracks.

Drying shrinkage is a complicated process, but in simple terms, the cement paste binder shrinks as larger pores within the paste lose moisture. As drying occurs, a meniscus forms at the air-water interface, and surface tension in this meniscus pulls the pore walls inward, causing the concrete to shrink. The test for shrinkage can be made as per ASTM C157 (Standard Test Method for Length Change of Hardened Hydraulic-Cement Mortar and Concrete). Figure 2 shows length change (%) versus time with SRA and without SRA.

The shrinkage-reducing admixture is unique because it works on water molecules, not the concrete structure. By reducing surface tension in the pore water, it reduces shrinkage forces on the pore structure when moisture leaves the concrete during drying. The percentage of shrinkage reduction for low and high dosage SRA for different days are given in Table 1.

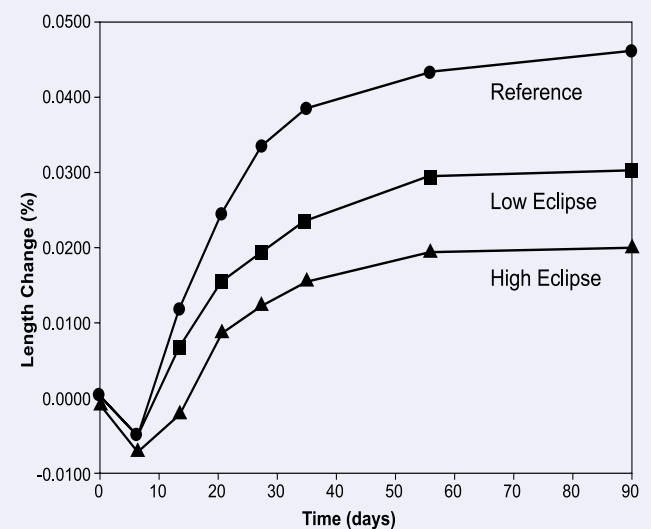


Figure 2 : Length Change (%) versus Time (Eclipse is SRA of Grace Construction Products, USA)

SRA Concrete versus Reference Concrete Shrinkage Performance

(expressed as % Shrinkage Reduction of Reference)

Table 1

	28 Days	90 Days	365 Days
Low dosage SRA	41	34	36
High dosage SRA	62	55	56

Effect of SRA on Compressive Strength:

There is an undesirable side effect as 2% SRA in the mix can reduce compressive strength by as much as 15% at 28 days. To offset this effect, it is recommended to add

enough superplasticizer to reduce mixing water by 7% to 10% while keeping cement content constant.

But studies by 'Brookes and Jiang' shows a reduction of 28% in 28-days compressive strength with an SRA of 1.5% by mass of cement addition with $w/c=0.42$ and cured at 100% RH against controlled specimens prepared without the SRA.

Also studies by 'Folliard and Berke' shows a reduction of 6% to 8% in 28-days compressive strength with a SRA of 1.5% addition, cured at 20°C and 100% RH for concretes with and without silica fume and w/s ratio of 0.35.

However studies by 'Benz, Geiker and Hansen' shows that a reduction of 15% and an increase of 14% in 7-days & 28-days compressive strength, with and without SRA respectively, with a w/s ratio of 0.35 containing 8% silica fume and 2% SRA, cured at 30°C and 100% RH. The higher 28-days compressive strength may be due to addition of silica fume along with controlled curing with higher internal RH during which silica fume reacts pozzolanically with the calcium hydroxide formed from the cement hydration, leading to higher degrees of reaction and higher strengths. But it seems that SRA does not contribute significantly in 28-days compressive strength.

Interaction between SRA and Cement Paste's Solution:

- The mixture of SRA and pore fluid forms an oil water-surfactant emulsion which may or may not be stable depending on the concentration of SRA. At some intermediate concentrations (7.5% to 15% for the synthetic pore solution), the emulsion becomes unstable and separates into two distinct phases; an SRA-dilute phase which contains approximately 7.5% SRA and a SRA-rich phase which contains the excess SRA (i.e., in excess of 7.5%). Below 7.5% and above 15% the emulsion is stable, clear and macroscopically homogeneous.
- SRA reduces the surface tension of pore fluid when added up to a threshold concentration (e.g., 7.5% for the synthetic pore solution). Beyond this critical threshold, further addition of SRA results in accumulation of surfactant molecules within the bulk solution rather than the solution-air interface. As such, beyond the critical threshold, further reduction in pore fluid's surface tension becomes marginal.
- The addition of SRA reduces the polarity of mixing water. This results in lowering the affinity of alkalis (e.g., K_2SO_4) to dissolve and ionize in the mixing water. Consequently, the

resulting pore fluid contains a smaller concentration of alkali ions compared to the pore fluid of a plain cement paste. The reduced alkalinity of the pore fluid has a direct impact on the rate of cement hydration and can contribute to retardation in hydration and strength development of concrete containing SRA.

- A delayed addition of SRA (e.g., addition of SRA to concrete at job site instead of addition during the initial mixing at concrete plant) can be beneficial in alleviating the hydration retardation. The absence of SRA in the original mixing water promotes the dissolution of alkalis. As a result, a higher alkali concentration may be achieved when SRA is added after the initial mixing.
- SRA concentration in the pore fluid increases as hydration progresses. This stems from the fact that water is consumed in the hydration process while SRA is not taken up by the hydration products (at least not at the same rate as water). As such, the concentration of SRA increases in the remained pore fluid. A similar phenomenon can occur when concrete is exposed to drying as water is removed by evaporation while SRA remains in the pore fluid. Figure 3 shows 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°C.

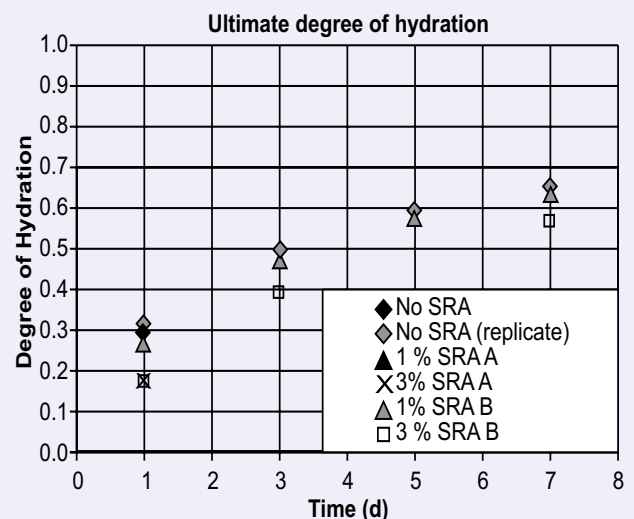


Figure 3 : Degree of hydration versus time

- Although the SRA accelerates the drying of bulk solutions, in cement paste with a w/c ratio=0.35, it actually reduces the measured drying rate.
- A change in the drying profile from uniform drying to a sharp drying front for $W/C = 0.35$ cement pastes exposed to drying conditions occurs.

- A decrease in the internal Relative Humidity (RH) reduction in low w/c ratio cement pastes and mortars cured under sealed conditions takes place. Fig. 4 shows differences in internal RH (Jensen and Hansen 1995) for ultrafine cement pastes (w/c=0.3) with and without SRA, cured under sealed conditions at 25°C.

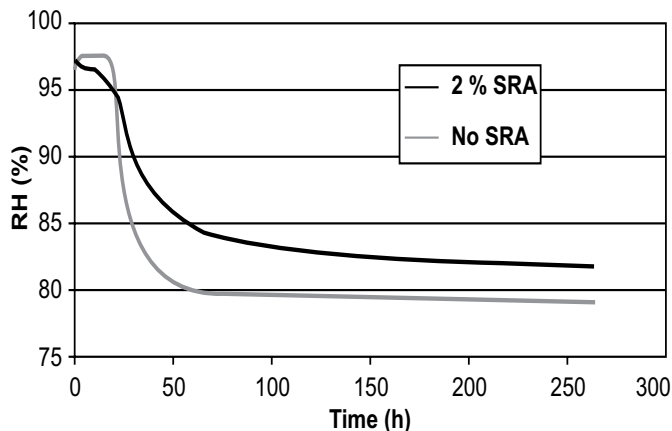


Figure 4 : RH versus time

- Also, a significant decrease in autogenous shrinkage in low w/c ratio mortars cured under sealed conditions occurs.

The above facts suggest that SRA is helpful for the mitigation of early-age cracking in low w/c ratio concretes and possibly for the design of improved curing systems and methodologies.



Figure 5 : Application of SRA Concrete

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 a 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 a 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.

The various application areas of SRAs are indoor slab on - grade concrete construction, bridge decks, parking garages, marine structures and containment structures. It can also be used to extend joint spacing and help reduce cracking in high value flooring.

Reference:

1. Bentz, D.P., Hansen, K.K., and Geiker, M.R. (2001a). "Shrinkage-Reducing Admixtures and Early Age Desiccation in Cement Pastes and Mortars," *Cement and Concrete Research*, 31 (7), 1075-1085.
2. Jensen, O.M., and Hansen, P.F. (1995a). "Autogenous Relative Humidity in Silica Fume Modified Cement Paste," *Advances in Cement Research*, 7 (25) 33-38.
3. J.J. Brooks, X. Jiang, The influence of chemical admixtures on re-strained drying shrinkage of concrete, in: V.M. Malhotra (Ed.), *Super-plasticizers and Other Chemical Admixtures in Concrete*, Am. Concr. Inst., SP 173 (1997) 249-265.
4. K.J. Folliard, N.S. Berke, Properties of high-performance concrete containing shrinkage-reducing admixtures, *Cem. Concr. Res.* 27 (9) (1997) 1357-1364.
5. Eclipse: Shrinkage Reducing Admixture, Technical Bulletin TB-1000, Grace Construction Products, USA