SINTEF Building and Infrastructure
COIN – Concrete Innovation Centre

Address: NO-7465 Trondheim
NORWAY
Location: Richard Birkelands vei 3
Telephone: +47 73 59 52 24
Fax: +47 73 59 71 36

Enterprise No.: NO 948 007 029 MVA

SINTEF REPORT

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COIN P1 Advanced cementing materials
SP 1.3.F Reduced cracking

Reduced cracking by modifying matrix with admixtures or additives

State of the art

AUTHOR(S)

Harald Justnes

CLIENT(S)

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS, Veidekke ASA and The Research Council of Norway

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ABSTRACT

This report presents a literature review on mitigation of autogenous and drying shrinkage cracking by shrinkage reducing agents (SRAs) as well as expansive additives.

The SRAs are often propylene glycol derivatives believed to function by lowering the surface tension of water and thereby the tensile stresses, but the mechanism is disputed.

Expansive agents are usually formulations that produce Ettringite, but reports are also found on hydroxide forming compound like lime (CaO) and Periclase (MgO).

There seems to be an interesting synergy in combinations of glycol based SRA and CaO expanding agent, which should be further investigated for practical applications within COIN.

A third class of expanding additives is gas forming admixtures, in particular aluminium powder generating hydrogen gas. However, these seem more difficult to control in terms of timing and expansion.

Fine LWA saturated with solutions shrinkage reducing admixtures that otherwise would interfere with the initial setting and hardening of cement, rather than plain water, for internal curing has not yet been fully exploited and is also recommended for pursuit in COIN.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Materials technology	Materialteknologi
GROUP 2	Concrete	Betong
SELECTED BY AUTHOR	Shrinkage cracking mitigation	Svinnriss kompensasjon
	Self-desiccation	Selvuttørking
	Admixtures	Tilsetningsstoffer

Foreword

COIN - Concrete Innovation Centre - is one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfill this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %). The present industrial partners are:

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS and Veidekke ASA.

For more information, see www.sintef.no/coin

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1 INTRODUCTION

Early-age cracking of concrete is a well known phenomenon that may seriously affect the service life of structures. High-performance concrete (HPC), in particular on horizontal surfaces such as bridge decks, is prone to cracking (Sellevold et al., 1994) even less than 12 hours after placing in spite of efforts to avoid drying. Kompen (1994) has summarized field experience in early-age cracking of HPC. The importance of autogenous shrinkage as a driving force may have been under-estimated in the past, but it is now widely accepted that it is an important cause for crack formation in HPC with w/(c+s) < 0.40 and fine supplementary cementing materials (SCMs). Autogenous shrinkage was in fact refered to as the “Achilles’ heel” of HPC by Kovler and Jensen (2005). Due to the low w/c, HPC is even more sensitive to drying shrinkage than normal concrete with higher w/c.

This state-of-the-art report (STAR) is an effort to summarize the research on mitigation of autogenous shrinkage and drying shrinkage by admixtures (e.g. shrinkage reducing agents reducing the surface tension of water menisci in pores) or addtivies (e.g. expanding products). Other mechanisms leading to early cracking, like thermal deformations due to heat of hydration, are omitted. Since the mechanism review focuses on paste and concrete matrix measurements, it is important to note that autogenous shrinkage of concrete and mortar will normally be less than predicted from their volume of paste due to restraint caused by the embedded aggregate and the release of absorbed water from the aggregate.

This STAR does not intend to encompass all factors of admixtures and additivies to mitigate autogeneous shrinkage, but merely the principles, materials for use and examples of applications.

2 OBJECTIVE

The overall objective of the activity in COIN where this report belongs is to make concrete with crack free surfaces, or at least make them invisible by distribution. The specific objective of this report is to elucidate how admixtures and additives may be used to mitigate shrinkage cracks and to review the state of the art of this topic.

3 DEFINITIONS AND MECHANISMS

RILEM Technical Committee 181-EAS (2002) issued a comprehensive report on early-age cracking in cementitious systems, where some terminology has been agreed upon:

Chemical shrinkage is the internal-microscopic volume reduction which is the result of the fact that the absolute volume of hydration products is smaller than that of the reacting constituents (cement and water). It is roughly proportional to the degree of hydration beyond the very early stage.

Autogenous shrinkage is the external-macroscopic (bulk) dimensional reduction of the cementitious system which occurs under isothermal conditions without exchange of moisture or any other substance with the surroundings (i.e., sealed curing). Autogenous shrinkage is usually driven by chemical shrinkage and the magnitudes of the two are roughly equal as long as the paste matrix is fluid-like. The autogenous shrinkage becomes smaller than the chemical shrinkage when the paste matrix has developed a self-supporting skeleton and the difference between them is manifested as internal *contraction pores* (roughly at the time of setting as shown by Justnes et al. (2000a) and reproduced in Fig. 1). Factors influencing autogenous shrinkage of cementitious systems have been reviewed by Justnes (2004).

Self-desiccation is the reduction of internal relative humidity in a sealed system when empty contraction pores are generated.

Chemical shrinkage is sometimes denoted as *total chemical shrinkage*, while autogenous shrinkage is denoted as *external chemical shrinkage* in line with the above definitions (e.g. Justnes et al. (1994)).

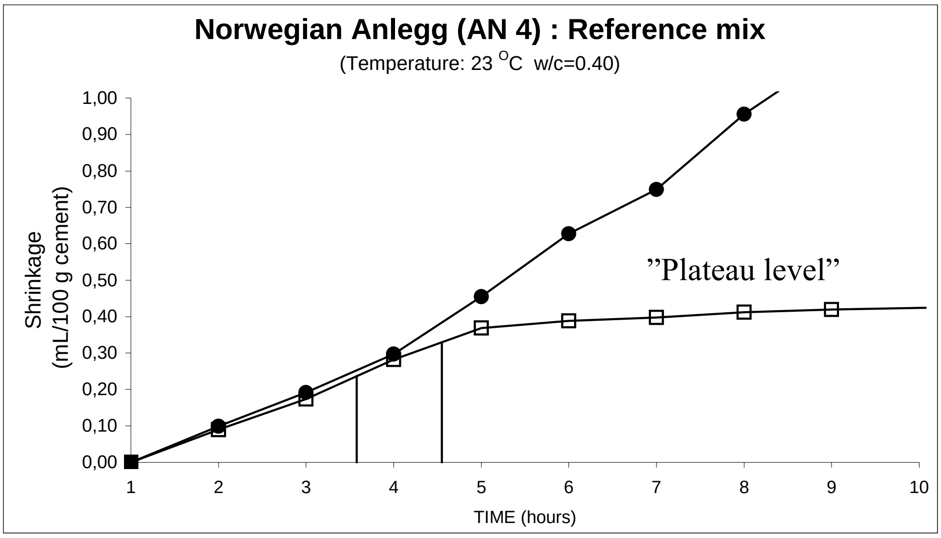

Fig 1 Chemical (●) and autogenous (□) shrinkage of cement paste (w/c = 0.40) compared with initial (left vertical line) and final (right vertical line) setting time by Vicat Needle. The gap between the two curves corresponds to the volume of contraction pores. (Justnes et al., 1994).

Chemical shrinkage is simply the difference in volume between hydration products and reactants. This is exemplified for the two phases with dominating reactivity during the first day (Justnes et al., 1998a); tricalcium aluminate together with gypsum in Eq. 1 and alite (C_3S) in Eq. 2. Knowing the density, ρ (g/ml), of reactants and products of a chemical reaction, it is possible from the molar weight, M (g/mol), of the involved compounds to calculate the volume change, ΔV (ml), pr mass, m (g), reactant remembering the basic relations $n = m \cdot M$ (mol) and $\rho = m/V$.

The shrinkage of the initial ettringite formation will then be;

$$C_3A \quad + \quad 3\,C\bar{S}H_2 \quad + \quad 26\,H \quad = \quad C_6A\bar{S}_3H_{32} \qquad [1]$$

m = 1.00 g	1.91	1.73	4.64
M =270.20 g/mol	172.17	18.02	1255.26
n = 3.70 mmol	11.10	96.20	3.70
ρ = 3.03 g/ml	2.32	0.998	1.78
V = 0.330 ml	0.823	1.733	2.607

$\Delta V = 2.607 - (0.330+0.823+1.733) = -0.273$ ml/g C_3A, while the chemical bound water is 1.73 g/g reacted C_3A, meaning that the chemical shrinkage is about 16 % of the chemically bound water.
The shrinkage of the alite reaction can be estimated in a similar manner, but the magnitude is strongly dependent of the composition and density of the CSH-gel formed. Justnes and Kjellsen

(2003) estimated the density of a 28 days CSH gel of composition $C_{4.7}S_{3.1}H_{5.9}$ to 2.49 g/ml, which leads to the chemical shrinkage of this balanced reaction;

$$C_3S + 3.39\ H = 0.325\ C_{4.7}S_{3.1}H_{5.9} + 1.48\ CH \qquad [2]$$

C_3S	3.39 H	0.325 $C_{4.7}S_{3.1}H_{5.9}$	1.48 CH
m = 1.00 g	0.268	0.786	0.480
M = 228.32 g/mol	18.02	552.3	74.09
n = 4.38 mmol	14.84	1.42	6.48
ρ = 3.15 g/ml	0.998	2.49	2.24
V = 0.317 ml	0.268	0.316	0.214

$\Delta V = (0.316+0.214) - (0.317+0.268) = -0.055$ ml/g C_3S, while the chemical bound water is 0.27 g/g C_3S, meaning that the chemical shrinkage is about 8 % of the chemical bound water. It is important to note that the chemical shrinkage of the C_3A reaction is much higher ($\approx$ 5 times) than the reaction of C_3S.

The chemical shrinkage of Portland cement being a mixture of a number of minerals, is in general considered to be about 0.06 ml/g cement (or about 25 % of the chemical bound water of 0.23 g/ g cement reacted according to Copeland and Hayes, 1953).

The total porosity of a cement paste based on 1 g cement of density 3.15 g/ml and water-to-cement ratio (w/c) of 0.40 can then be calculated as follows assuming a degree of hydration α = 0.30 (30 %) for the first day;
Chemical bound water = $0.23 \cdot 0.30 = 0.069$ g/g cement
Physically bound water = $0.17 \cdot 0.30 = 0.051$ g/g cement
Liquid water with density 1.0 g/ml = capillary porosity = $0.40-(0.069+0.051) = 0.28$ ml/g cement
Empty contraction pores (i.e. vacuum) = $0.25 \cdot 0.069 = 0.017$ ml/g cement
Total porosity is then $(0.280+0.017)$ ml$\cdot$100 vol%/$(1/3.15 + 0.4/1)$ ml = 41.4 vol%

The total porosity after 1 day hydration is distributed between 39.0 vol% water filled capillaries and 2.4 vol% empty capillary pores. The vacuum in the empty pores can be relieved by either shrinking the concrete in its plastic stage or by sucking air from the surface. Nevertheless, water menisci will be created in the pores and tension induced that potentially will lead to shrinkage cracks.

The basic mechanisms of autogenous shrinkage were recently evaluated by Lura et al. (2003). Other contributions to understanding the mechanisms have been given by Wittmann (2001), Mitani et al. (2001), and Thomas and Jennings (2001). The basic mechanisms are actually more or less outlined in the preceding definitions of chemical shrinkage, autogenous shrinkage, and self-desiccation.

Before setting, when chemical shrinkage and autogenous shrinkage are equal, the external volume change will be followed by a stretched, elastic rubber membrane if used. See Justnes et al. (1994) for detailed experimental set-up. In a uni-axial, horizontal dilatometry set-up, this external volume reduction would be manifested as subsidence and usually not recorded, or the measurement starts after setting and demolding.

After setting there will be a formation of empty contraction pores that initially are empty and that are forming an under-pressure. At this stage, the pore connectivity is quite high, so the water will re-distribute so the coarsest pores will empty first. Koenders and de Rooji (2003) discussed internal moisture flow by microstructural contraction. They concluded that the empty pores will have a minimum pressure equal to the partial pressure of water in equilibrium with the pore water and some dissolved air going into the gas phase when the pressure is reduced (i.e., solubility of gas is proportional to the pressure). The magnitude of this under-pressure is governed by the amount of solute in the water according to Raoult's law;

$P/P_0 = X$ (= relative humidity in case of water) [3]

where P = is partial pressure over the solution, P_0 = the pressure over pure solvent, and X is the molar fraction of free solvent in the solution. Note that in the case of water, water molecules coordinating around the ions also have to be subtracted in calculations. Water in fresh paste contains in general about 0.1 M alkali hydroxides and some sulphates that will ion-exchange to hydroxides rather quickly. Lura et al. (2003) measured an initial RH of 0.98 (i.e. P/P_0 in Eq. 3) due to this effect, while Page and Vennesland (1983) measured 0.967 for the composition of the pore solution extracted from a w/c = 0.45 paste after 2 months. However, the effect of Raoult's law will first become an important factor when solutions are getting concentrated (achievable for w/c < 0.4) where RH on the order of 0.4 may be obtained easily. This is the same principle used to obtain constant humidity by saturated salt solutions. Concentrated KOH gives, for instance, 9 % RH at 20°C.

However, at the stage of concentrated salt solutions, the pore refinement has progressed for a while. Before that, the equilibrium pressure of water over the meniscus in the coarsest pore filled with water (i.e., assuming that water will redistribute easily) will dominate in accordance with the Kelvin equation for cylindrical pores;

$$\ln\left(\frac{P}{P_0}\right) = \frac{-2\cdot\gamma\cdot M\cdot\cos\theta}{\rho\cdot r\cdot R\cdot T} \qquad [4]$$

where γ = surface tension of water (0.073 N/m in pure water and 0.055 N/m for a pore fluid according to Jensen (1993)), M = molar mass of water (18.02 g/mol), θ = the contact angle between water and solids (close to 0°), ρ = density of water (approx. 1,000 kg/m^3), r = the radius of the meniscus (m), R = the ideal gas constant (8.314 J/mol·K), and T = the absolute temperature (K).

If the effect on relative humidity by dissolved salts according to Raoult's law in Eq. 3 could be isolated from the effect of the water meniscii according to the Kelvin equation (Eq. 4), the radius, r, of the coarsest pore filled with water could be calculated from simple RH measurements. This could be used to calculate the tensile stress in the pore fluid according to the La Place law for cylindrical pores;

$\sigma_{Cap} = 2\cdot\gamma/r$ [5]

This tension stress of capillary water, σ_{Cap}, is generally thought to be the major driving force of autogenous shrinkage. Jensen (1993) claimed that the measured relative humidity could be approximated by the product of the contributions from Eqs. 3 and 4. This was also used by Lura et al. (2003) who also claimed that the contribution of dissolved salts in accordance with Raoult's law (Eq. 1) was constant to 2 % RH reduction throughout hydration. The present author will argue that these assumptions are not correct, and the fit between observed and calculated linear shrinkage by Lura et al. (2003) showed a large deviation when RH caused by meniscus formation fell below 97 %.

There will be an under-pressure in the empty pores, which for a sealed case without air bubbles and dissolved air can not exceed the pressure of water vapour above free water (23 torr at 25 °C), but will be much less due to the effects described by Eqs. 2 and 4.

The pressure drop in the paste can also be measured directly by a method developed by Radochea (1992), using a water filled tube attached to a pressure transducer. The tension recorded in the water in the tube is believed to reflect the tensile stress of the pore water (σ_{cap} in Eq. 5), which in turn is transferred to the pore walls creating shrinkage. Examples of pressure drop in pastes of cements of different fineness are shown by Sellevold et al. (1994) and the Radochea (1992) device was later used by Hammer (2001). Generally at first, in the experiment with the water filled tube immersed into the paste ,the pressure equals the hydrostatic pressure of the suspended paste (i.e. a column of cement paste) according to

$$P = \rho \cdot g \cdot h \qquad [6]$$

where ρ = the density of the paste (kg/m^3), g = gravitational constant and h = depth of measurement below surface (m).

The pressure drops slowly as a function of time to a level corresponding to a column of same height of water percolating through the network of selfsupporting particles (i.e., only ρ changes from about 1,900 to 1,000 kg/m^3 in this “segregation” process of hydrating particles). Thereafter, there is a plateau until the first water menisci and vapour filled pores are formed roughly at the point of setting, followed by a gradually capillary water tension increase at first, which is rapidly accelerating. As seen in Fig. 2, the time from setting to achieve a pore water tension of 100 mm “hanging” (i.e., negative) water column is in the order of 1 hour, and from there it may take only half an hour to increase the pore water tension further to a 500 mm negative water column, and even less. Note that at such a low tension, the water vapour pressure is not affected much, so water may evaporate from coarser pores, be transported as vapour, and condensate in smaller pores. For comparison, it will take a pore water tension build-up corresponding to a 10^6 mm water column (i.e., 1 km water column or 100 atm) before the relative humidity is reduced to 93 % (according to Eqs. 4 and 5).

Charron et al. (2001) compared autgenous shrinkage by a volumetric method with that of a linear dilatometric method for mortars. They found, like many others, that there is a large discrepancy between the two methods, where the dilatometry method gives an order of magnitude less shrinkage after setting, even when the results are made comparable by multiplying the linear measurements by a factor of 3 to take into account all principal directions. The authors did not find any good arguments for this observation.

According to the present author, one cannot rule out that the samples for linear measurements are not sealed properly, even when they are covered by wraps to avoid evaporation (with the exception of the corregated tubes used by Jensen (1993)). The pressure in the pores will then soon approach atmospheric by air being sucked in to them. The vacuum contribution to shrinkage will then be removed. The capillary tension due to menisci will, however, still be in place. The capillary tension can be lowered due to capillary condensation if evaporation is hindered by placing the sample in a chamber of high humidity. This could be an important contribution to explaining the discrepancy between volumetric and linear shrinkage measurements.

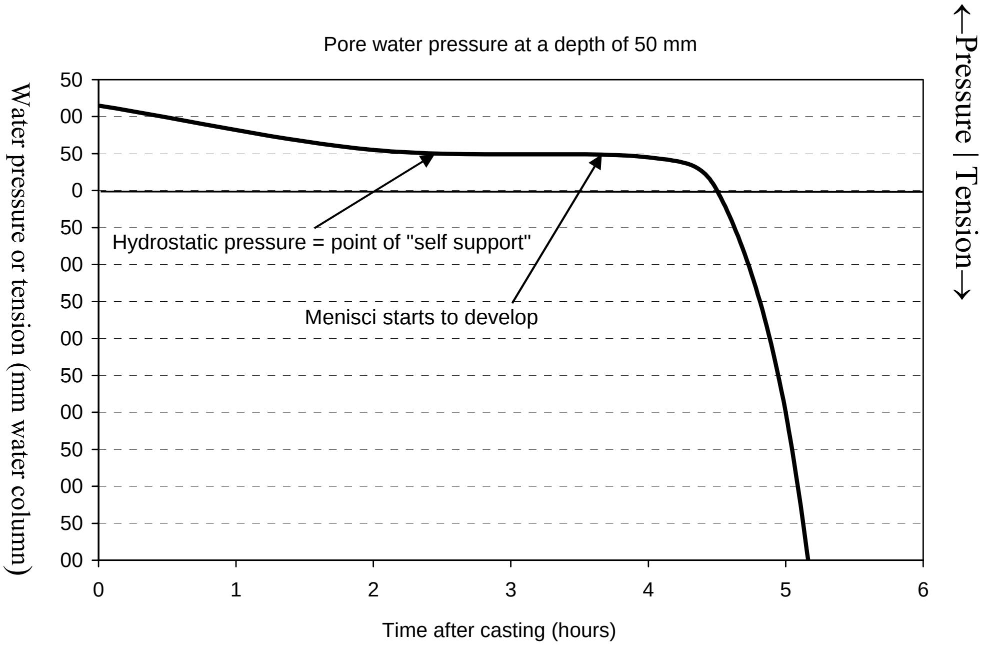

Fig. 2 Principle for interpretation of the development of pore water pressure and tension in cement paste with the measuring tube at 50 mm depth, after Hammer (2001).

The smaller autogenous shrinkage observed by linear methods relative to volumetric methods was discussed in detail by Hammer et al. (2001). They mentioned factors like 1) friction between sample and substrate, 2) bleeding and re-suction of bleed water creating expansion and 3) thermal expansion effects as the three important factores. In particular the 3rd effect, since temperature rise due to heat of hydration in non-submersed samples is difficult to avoid, and it may reach as much as 10°C above ambient temperature. This effect may actually be the reason for the difference (factor of 10) observed by Charron et al. (2001) since they compared the residual shrinkage after the thermal expansion peak for the sample in the linear experiment with that of the autogenous volumetric autogenous shrinkage of a submersed specimen. Since hydration rate is roughly increased by a factor of 2 per 10°C increase, the sample for the linear measurement would have been more mature at the point of comparison.

Since autogeneous shrinkage cracking is most prone for HPC and the characteristics of HPC are low w/c, use of supplementary cementing materials (SCMs) and use of plasticizers, a few pages should be spent on these three items.

Justnes et al. (1996) measured the effect of w/c on chemical and autogenous shrinkage of two different cement pastes. Chemical shrinkage (water saturated curing) was largely independent of w/c over the investigated w/c range (0.3 to 0.50) and time (0 to 48 h). Autogenous shrinkage (sealed curing) against time curves matched the chemical shrinkage crurves until a plateau level, was reached (see Fig. 1). This level was largely independent of w/c when shrinkage was expressed as mL/100 g cement, meaning that the volumetric autogenous shrinkage increases with decreasing w/c (since there is more cement per unit volume). There was also a tendency towards a more rapid fluid to solid skeleton transition at higher w/c and a slower more gradual transition at lower w/c.

Justnes et al. (2000b) investigated the effect of w/c in addition to the effect of admixtures on autogenous shrinkage. It was confirmed that the magnitude of autogenous shrinkage was only marginally (within 0.1 mL/100 g cement) influenced by w/c (0.3, 0.4 and 0.5) when measured as mL/100 g cement. A similar conclusion was drawn from an independent study by Justnes et al. (2000a).

Charron et al. (2001) measured the linear autogenous deformation on mortar with w/c = 0.45 and 0.35 and found a larger shrinkage for the lower w/c.

Justnes et al. (1999) tested the effect of 10 % precipitated calcium carbonate and silica fume on the chemical and autogenous shrinkage of pastes with different cements. The influence of the mineral additives on chemical shrinkage rate was dependent on cement type; sometimes accelerating and sometimes equal to the reference. The effect of mineral additives on autogenous shrinkage was also depending on the cement type; sometimes increasing the plateau level and sometimes leaving it equal relative to the reference. A higher plateau level for pastes with fine mineral additives can be explained by pore refinement and menisci formed by initial contraction pores leading to stronger forces. Thus, more hydration is required to create stronger network to resist them.

Justnes et al. (1998) tested the effect of silica fume (SF) replacing cement at dosages of 0.0, 2.6, 5.3, 11, 20 and 25 % on chemical and autogenous shrinkage up to 7 days. Deformation was reported as mL/100 g cement, which means that a lower, equal or higher value correspond to a pozzolanic reaction that expands, has no volume change, or shrinks, respectively. Chemical shrinkage increased with increasing SF dosage, showing that the pozzolanic reaction leads to shrinkage, as expected. The autogenous shrinkage showed (see Fig. 3) equal plateau levels for SF replacements up to 11 %, while 20 and 25 % SF successively increased the autogenous shrinkage. This observation was explained by the particle packing of the system; up to 11 % SF replacement of cement (about 0.15 μm size) fills in the gaps formed between the irregular cement grains (average size 15 μm), maintaing close contact between individual cement grains. About the same amount of hydration is then required to form a hydrate network strong enough to resist the contracting forces. With greater SF replacements, cement grains are dispersed in excess silica fume and a higher degree of hydration is required to form such a network.

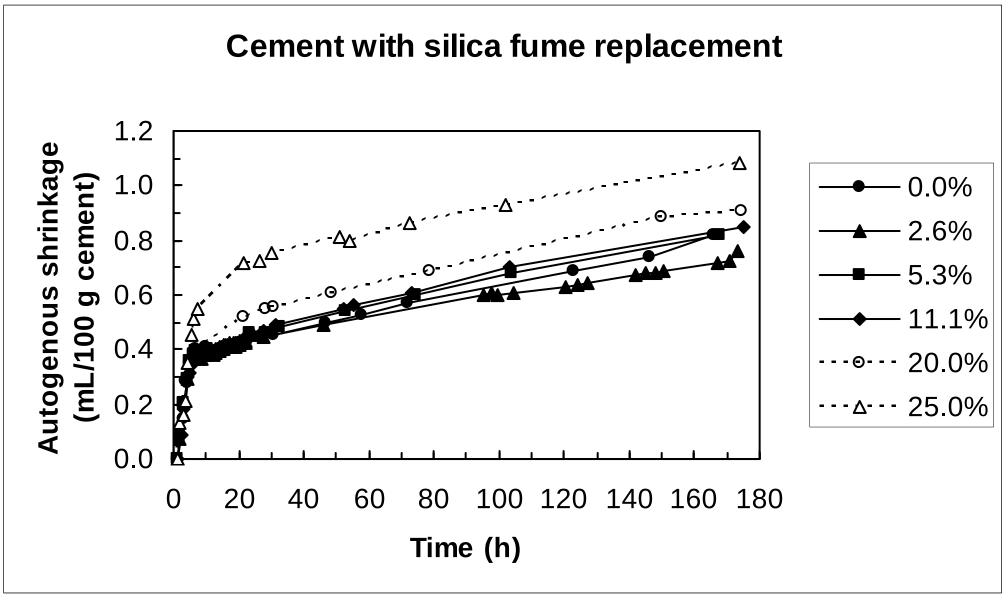

Fig. 3 Autogenous shrinkage of cement pastes as a function of silica fume replacement (after Justnes (1998)).

Justnes et al. (1998) investigated the chemical shrinkage of the pozzolanic reaction between lime and silica fume and between lime and class F fly ash without cement. The effects of lime/silica ratio, pH, and water content of these pastes were investigated. The rate of chemical shrinkage decreased with increasing pH of SF with lime addition, in spite of the catalytic necessity of alkalis for rapid pozzolanic reaction. This was explained by the fact that increasing pH (12.5, 13.0, and 13.5) decreases the solubility of calcium hydroxide (CH) due to the common ion effect assuming dissolution of CH is followed by the precipitation of CSH as the rate limiting step. The chemical shrinkage was relatively unaffected by mass ratios *w/c+s* in the range 0.8 to 1.2 and by molar C/S ratios in the range 0.7 to 1.5. On the other hand, the rate of chemical shrinkage increased with increasing pH for the lime-fly ash mixture indicating that the dissolution of the glassy aluminosilicate phase by alkalis is rate determining for this pozzolanic reaction. The chemical shrinkage of the pozzolanic reactions was crudely estimated to be 8.8 mL/100 g of reacted SF and 10.0 mL/ 100 g of reacted fly ash, as compared to 6.3 mL/100 g for hydrated cement. However, taking into account density differences (2,200 kg/m^3 for silica fume and 3,150 kg/m^3 for cement), the chemical shrinkage was roughly equal when expressed per unit volume of cementing material.

Jensen and Hansen (1996) studied the influence of SF on linear autogenous shrinkage of cementitious paste (w/c = 0.30) in horizontal corrugated plastic tubes for two different cement types and 0, 5, 10, and 20 % SF addition. Note that with addition, rather than replacement, *w/c+s* is reduced from 0.30 to 0.25 for 20 % SF addition. The effect of silica fume was increased linear autogenous deformation with increasing addition rate. Particularly surprising was the large increase in autogenous shrinkage from 0 to 5 % SF addition, while the effect from 10 to 20 % was minor. Note that any minor bleeding by the reference paste would hamper the results, since suction of bleed water will counteract shrinkage and even may lead to swelling. However, both the effective lowering of *w/cm* and refinement of the pores by improved particle packing will lead to earlier meniscus formation in finer pores and thereby create higher tensile stresses. Reduced tensile strain capacity of the paste with SF relative to the magnitude of the tensile stress build-up may explain the results.

Justnes et al. (2000c) investigated the effect of the three types of plasticizers (lignosulphonate, naphtalene sulphonate-formaldehyde condensate and sulphonated melamine-formaldehyde condensate) in 3 different dosages on chemical and autogenous shrinkage of cement paste made from 5 types of portland cement. They concluded that the plateau level of autogenous shrinkage was independent of admixture type, and was the same as for the reference paste without admixtures, as long as the specimens were rotated (i.e., undisturbed by bleeding). Furthermore, the admixtures did not directly influence the chemical shrinkage in a way that should indicate a higher risk of cracking. However, the retardation of early hydration and setting of cement by lignosulphonate could allow a longer period of evaporation of water from floors and bridge decks in practice. For this reason mixtures with lignosulphonates might be more prone to form drying shrinkage cracks. These conclusions were confirmed by Justnes et al. (2000b).

Drying shrinkage occurs due to formation of menisci created in the pores when concrete looses water from its surface to the surroundings. The tension stress of the capillary water, σ_{Cap}, in these pores follows also Eq. 5, and is generally thought to be the major driving force of drying shrinkage. However, while autogenous shrinkage acts evenly throughout the cross-section of a specimen leading to direct tensile strresses, drying shrinkage forms a gradient from the surface inwards resulting in flexural stress which lead to “curling” of plates etc. Drying shrinkage is enhanced by low relative humidity (RH), high temperatures and high wind speed over the concrete surface. Countermeasures applied to the surface after set is watering, plastic foil coverage, curing membranes etc, but the topic of this report is admixtures and additives added to the bulk volume of concrete. Baroghel-Bouny (1997) pointed out the similarities between autogenous and dryinmg shrinkage.

Bentz (2007) reviewed the early age properties of cement based materials, including the different forms of shrinkage and their counter-measures.

4 SHRINKAGE MITIGATION BY ADMIXTURES AND ADDITIVES

Two principly different measures for mitigating autogenous and drying shrinkage (Bentz, 2007) are reviewed namely admixtures believed to modify the surface tension of water to reduce the stresses formed by menisci in partially emptied capillary pores and expanding additives that are meant to counteract the shrinkage stresses. A third possibile measure, internal curing, is reported in a separate STAR.

4.1 Admixtures modifying surface tension of water

The term shrinkage reducing admixtures (SRAs) referres in literature to organic admixtures (usually propylene glycol ether derivatives) that are generally believed to function by reducing the surfce tension of water, γ, in water. In accordance with Eq. 5, a 30 % reduction in surface tension would give a 30 % reduction in tensile stress. This hypothesized reduction in autogenous shrinkage for systems containing SRA has been verified experimentally (e.g. Shoya and Dugita, 1989, Shah et al., 1992, Weiss et al., 1997, Shah et al., 1998, Bentz et al., 2002, Rongbing and Jian, 2005, Esping and Löfgren, 2006, and Sant et al., 2007) as exemplified in Fig. 4 by Bentz et al., 2001a. However, the actual mechanisms of how SRAs function is still debated as will be illustrated by the following review.

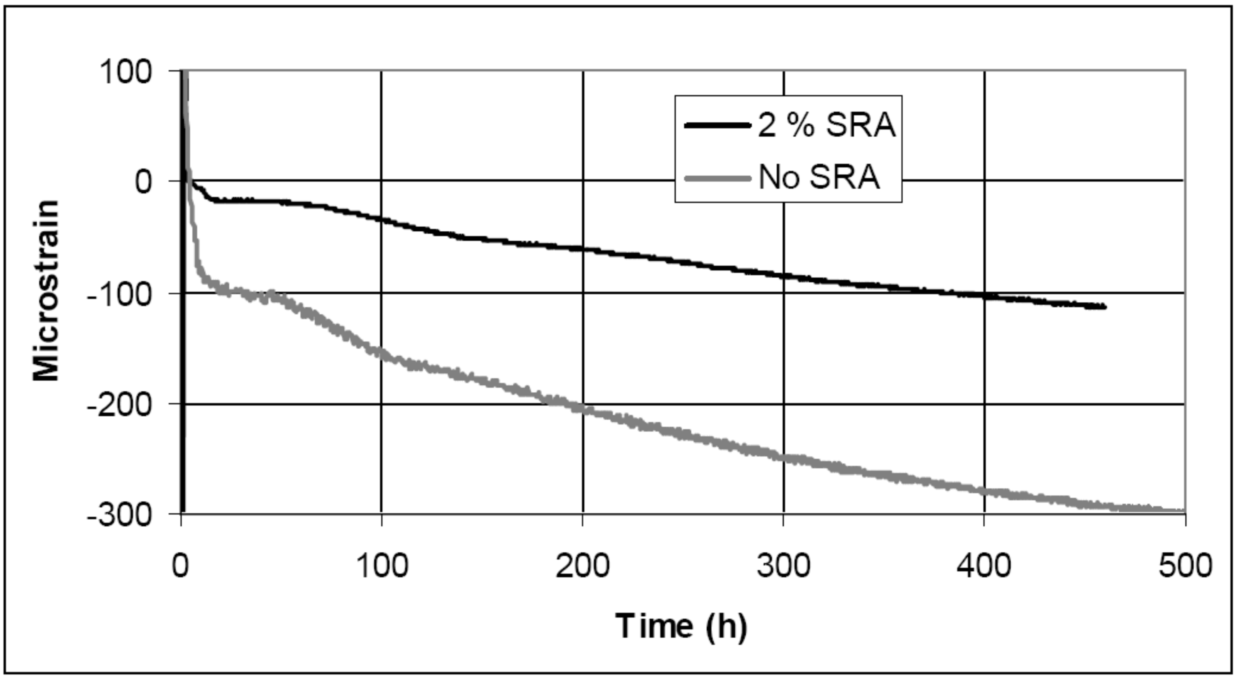

Fig. 4 Differences in autogenous deformation of mortars (w/cm = 0.35) with and without SRA, cured under sealed conditions at 30°C (Bentz et al., 2001).

First employed in Japan over twenty years ago as published by Sato et al. (1983), SRAs have been utilized to reduce drying shrinkage for the past ten years or so in the U.S. (Folliard and Berke, 1997, and Nmai et al., 1998). The addition of a few percent SRA (by mass of cement) can reduce the measured surface tension of the concrete pore solution by a factor of two according to e.g. Ai and Young (1997), Bentz et al. (2001a), Lura et al. (2005) and Pease (2005). Pease (2005) found that the surface tension of water can be calculated for distilled water with SRA addition by;

$$\gamma_{sol} = \gamma_w \cdot \left[1 - \delta \cdot \ln\left(\frac{C_{SRA}}{\phi}\right)\right] \text{ when } C_{SRA} < 15\% \qquad [7]$$

$$\gamma_{sol} = \gamma_{sol,\,sat} \text{ when } C_{SRA} > 15\%$$

where γ_{sol} (N/m) is the surface tension of the solution of SRA in distilled water, γ_w (N/m) is the surface tension of distilled water, C_{SRA} (%) is the concentration of SRA in water, δ (-) is a constant characteristic of a series of organic compounds similar in structure (i.e. SRA) and ϕ (%) is a constant of an individual compound.

Pease (2005) found that the surface tension reached a minimum value at SRA concentrations beyond 15 % and tabulated the values of δ, ϕ and $\gamma_{sol,\,sat}$ for a number of compounds. Apparently the saturation concentration is dependent on the class of compounds, as Ai and Young (1997) found a saturation dosage of only 5 % for their SRA, reducing the surface tension to 37 from 72 dynes/cm for pure water.

Another potentially different mechanism discussed in the literature, is the effect of SRA on the mass loss during drying. As shown in Fig. 5, according to X-ray transmission measurements by Bentz et al. (2001a), the drying profile generated in the presence of an SRA is vastly different from that generated in a system without SRA (as reproduced in Fig. 6, but note that the w/c is higher) at early ages (≤ 8 h). Bentz et al. (2001a) describes the effect as SRA resulting in a drying front penetrating into the specimen from the surface exposed to the drying environment, while the interior of the specimen remains saturated. Apparently, as pore solution is initially drawn by capillary forces to the surface to evaporate, the remaining solution at the surface will contain a greater concentration of SRA than the solution within the interior of the specimen.

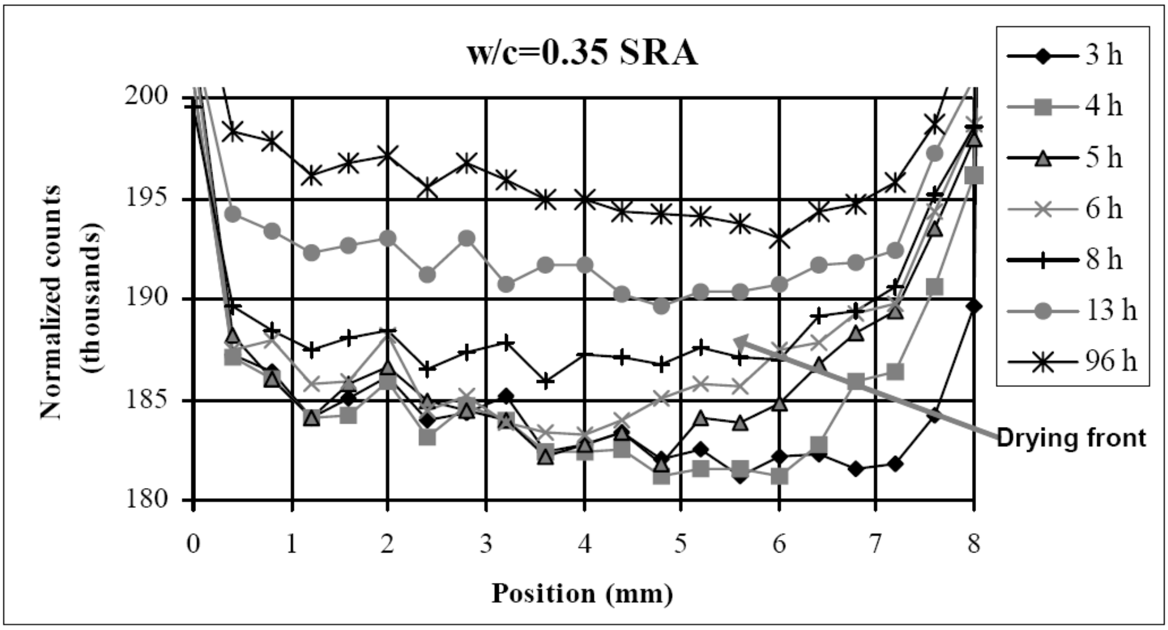

Fig. 5 Normalized counts for X-rays transmitted through a *w/c*=0.35 portland cement paste with a 2 % SRA addition by mass of cement, immediately exposed to drying conditions (23°C and 50 % RH), as a function of curing time (3 h to 96 h) and depth. Top of specimen is located at about 8 mm (Bentz et al., 2001a).

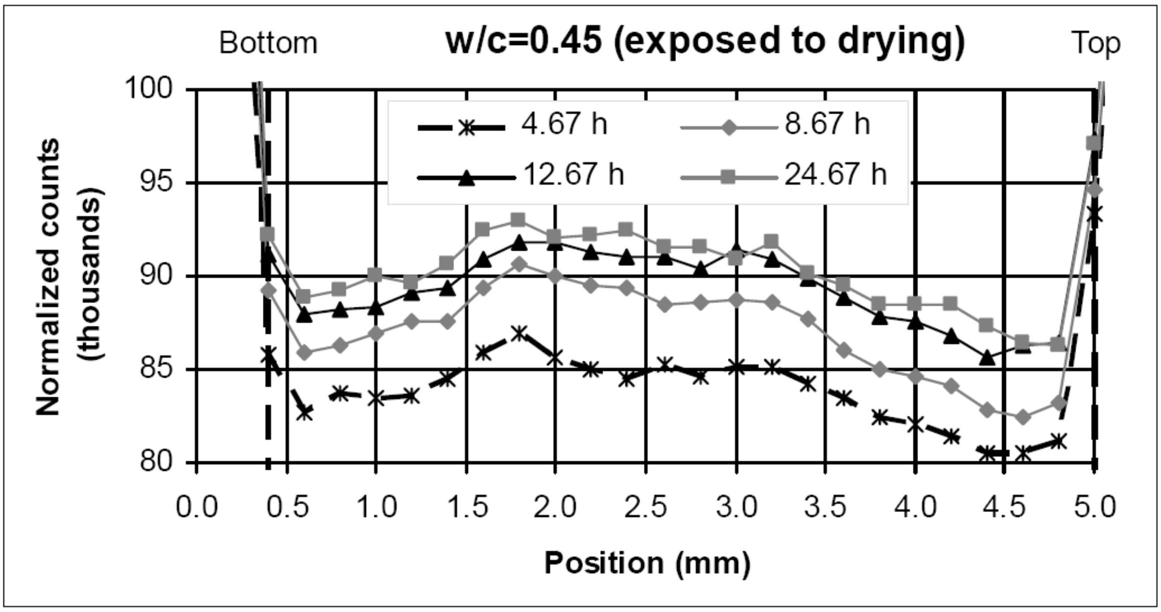

Fig. 6 Normalized counts for X-rays transmitted through a w/c=0.45 portland cement paste immediately exposed to drying conditions (23°C and 50 % RH), as a function of curing time (4.67 h, 8.67 h, 12.67 h, or 24.67 h) and depth. Top of specimen is located at about 5 mm (Bentz and Hansen, 2000).

Just as water is drawn from a coarser pore system to a finer one in bi-layer composites (Bentz et al., 2001b) due to the differential in capillary forces, the surface layer will no longer be able to "pull" water from the higher surface tension water below; confirmatory measurements of these phenomena have been made previously on bi-layer (SRA over no SRA and no SRA over SRA) composite specimens (Bentz et al., 2001a). This results in a reduced evaporation *rate* in a system with an SRA relative to a system with no SRA addition (Bentz et al., 2001a, and Esping and Löfgren, 2006). In regards to pore solution movement within a specimen, it is also worth mentioning that the measured viscosity of a typical 10 % SRA solution in distilled water is about 50 % higher than that of distilled water alone (Bentz, 2006b), implying a slower internal "flow rate". As indicated by Lura et al. (2006), the addition of the SRA thus results in "less evaporation, reduced settlement, reduced capillary tension, and lower crack-inducing stresses at the topmost layer of the mortar," consistent with the experimental results of Esping and Löfgren (2006) for self-consolidating concretes. These effects all combine to provide a reduction in the propensity to form plastic shrinkage cracks when exposed to a drying environment (Lura et al., 2006, and Esping and Löfgren, 2006). Bentz (2005b) showed that a similar reduction in evaporative water loss can be achieved by surface application of an SRA solution (10 % or 20 % by mass in water) as a curing solution. Timely application of the SRA solution to the top surface of mortars being exposed to a 50 % RH environment resulted in significant reductions in subsequent evaporative water loss and significant increases in the degree of hydration achieved in the specimens at longer ages (Bentz, 2005b).

There has been some confusion in literature concerning mass loss during drying with and without SRA. Sant et al. (2007) measured the 7 days mass loss and shrinkage strain for paste (w/c = 0.30) with and without 20 % silica fume and with and without 5 % SRA at different relative humidities (RH) as reproduced in Figs. 7 and 8. They found no difference in mass loss, but reduced shrinkage strain for RH ≤ 70%. However, note that a 7 days mass loss does not say anything about the mass loss *rates* at earlier ages.

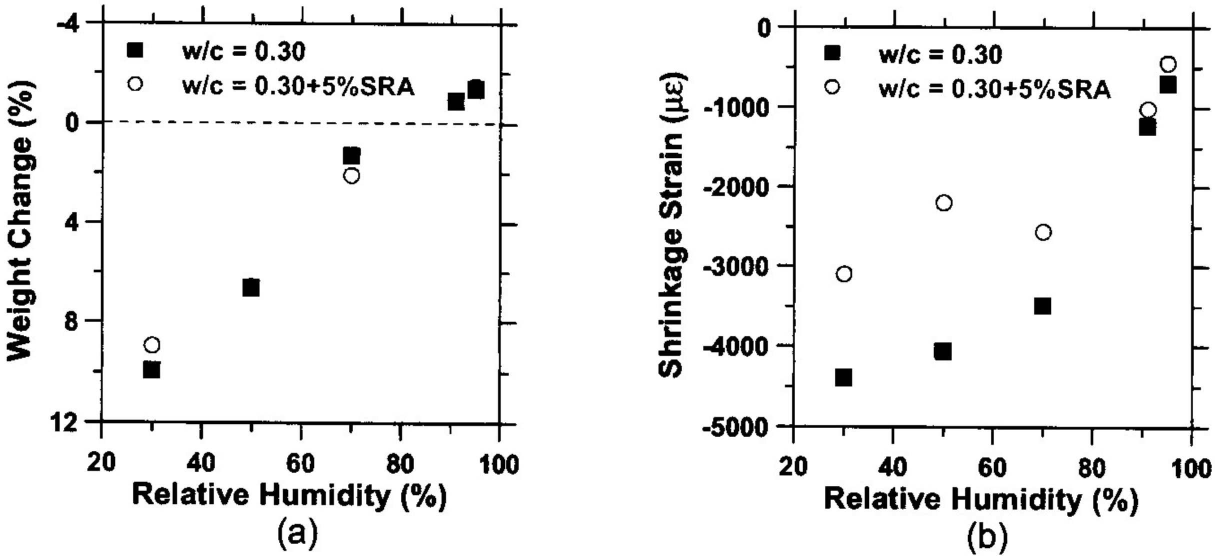

Fig.7 (a) Weight change (%) and (b) shrinkage strain measured on paste specimens (w/c = 0.30) with (○) and without (■) 5 % SRA exposed to drying at different RH for 7 days (Sant et al., 2007)

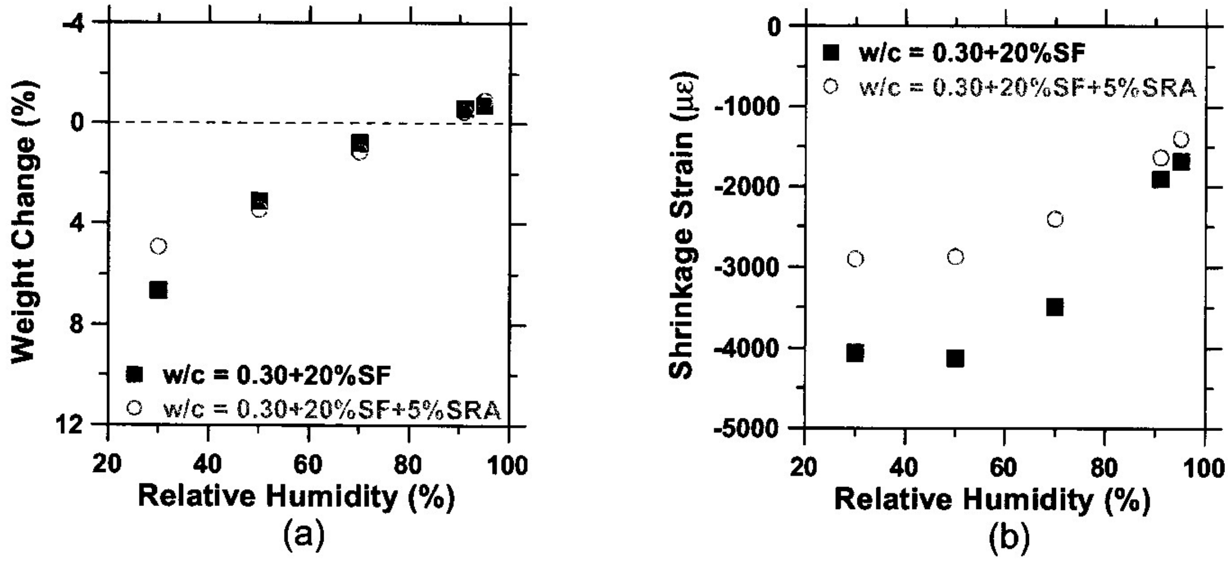

Fig.8 (a) Weight change (%) and (b) shrinkage strain measured on paste specimens (w/c = 0.30) with 20 % silica fume and with (○) and without (■) 5 % SRA exposed to drying at different RH for 7 days (Sant et al., 2007).

Ai and Young (1997) actually found an increased mass loss rate for the first 50 h due to their SRA addition. The mass loss difference persisted until the last measuring point at 10 days (12 % vs. 9 %) while the shrinkage was less (0.3 % vs. 0.4 %) than without SRA. They measured also a change in pore size distribution by MIP (mercury intrusion porosimetry), showing that the SRA gave a higher fraction of macro pores. This can explain the higher mass loss since shrinkage is associated with water removal from the meso pores and not the macro pores as the tension stress is inversely proportional to the radius of the pore s with menisci (see Eq. 5). Palacios and Puertas (2007) also showed that their SRA lead to a coarsening of the pore structure (increase in the 1.0-0.1 μm range) in their alkali activated slag paste and mortar system. This effect was pointed out as a secondary mechanism for the performance of SRA. Chen et al. (2007) also found that their SRA gave more mass loss from mortar compared to the reference.

SRA is actually theoretically expected to give a higher mass loss rate since reduced surface tension gives increased RH (i.e. P/P_0) according to Eq. 4 and it was proven for bulk water solution by Bentz et al (2001a). Any retardation of cement by SRA would also give increased early mass loss rate and reduced shrinkage due to coarser pores, although retardation will differ from one compound to another, which can explain the different results reported in the literature. In spite of higher evaporation from bulk water with SRA, Bentz et al (2001a) found marginally less evaporation from cement paste with the same SRA and they explained this seemingly discrepancy in evaporation from bulk water vs. mortar by a computer model.

Bettencourt Ribeiro et al. (2007) tested the influence of two SRAs in different dosages on shrinkage, compressive strength and mass loss during drying. One SRA was based on high molecular weight polyglycol and the other on alkylether. They also measured the influence of the SRAs on the reduction of surface tension of water, but found no proportionality with the reduced autogenous shrinkage or drying shrinkage. The negative effects of the SRAs were that they tended to delay setting and decrease long term strength.

Palacios and Puertas (2005) reported that their SRA was stable in the highly alkaline water of their alkali-activated slag pastes and mortars, while the polycarboxylate based super-plasticizer disintegrated by losing the grafted polyether side chains. Nakanishi et al. (2003) actually designed a polycarboxylate based superplasticizer that will split off SRA molecules in the alkaline environment of a cement paste. The effect was not so great, probably since the dosage was much smaller than dedicated SRA additions.

Corinaldesi and Moriconi (2007) tested polycarboxylate based super-plasticizes (PC) with incorporated SRA-groups on concrete with recycled aggregate known to shrink more than concrete with ordinary aggregate. The best PC-SRA resulted in 60% less shrinkage after 70 days compared to concrete with ordinary PC.

Sugamata et al. (2007) made blends of PC and SRA rather than integrated PC-SRA molecules. They were able to reduce autogenous shrinkage by 15-30% and drying shrinkage by 3-25%. However, the reported some negative side effects of SRA additions; 1) the required SP dosage increased by 5-10 % to obtain prescribed slump flow, 2) setting time was retarded by ½-1 h, compressive strength decreased by 1-5 MPa from the 150-170 MPa compressive strength of the ultra-high strength concrete reference.

There is a lot of secrecy in the literature about the actual composition of the SRAs and many of the test reports simply states their sales name. Rongbing and Jian (2005) shed some light on this as they formed SRA by reacting 2-butoxy ethanol with either ethylene or propylene oxide through a catalysed ethoxylation. Many authors (e.g. Maltese et al., 2005) refer to the SRAs as propylene glycol ethers, but only one paper (Collepardi et al., 2005) actually identified their SRA to be neopentil glycol; $(CH_2)_2\text{-}C\text{-}(CH_2OH)_2$.

Apart from mitigating both autogenous *and* drying shrinkage (Berke and Li, 2003, and Rongbing and Jian, 2005), SRAs has some negative side effects. Ribeiro et al. (2003) found that SRA gave some reduced strength, in particular early hydration stages (2 days) for low quality concrete mixes (-31 % in the worst case) indicating retardation. Shah et al. (1992) also found reduced strength by addition of SRA. In fact, if the capillary forces are reduced by SRA one would expect at least reduced strength in direct tension even at higher ages, if not compression. Brooks and Jiang (1997) found that their SRA reduced tensile strength from 3.5 to 2.5 MPa (-29 %) while the compressive strength was reduced from 68 to 54 MPa (-21 %) at 28 days and the flexural strength was lowered from 6.8 to 5.4 MPa (-21 %).

A factor that is not much discussed in the literature is that the SRA may stay in solution and the effective concentration in the pore water will increase as the hydration proceeds. Ai and young (1997) showed that their SRA did not adsorb to neither dry nor hydrated cement. A 2 % SRA addition of cement mass to a paste of w/c = 0.40 will for instance initially have a concentration of 5 % in the mix water, but will increase to 7 % once the degree of hydration has reached 30 % provided there is no adsorption to the hydration products. The higher the degree of hydration or the lower the w/c, the higher will the effective concentration of SRA be in the pore water be.

Berke et al (2003) pointed out another negative effect of many SRAs; that they are incompatible with air-entraining agents or hamper the formation of good air void systems needed for freezing and thawing resistance. However, they managed to design a SRA that worked well together with air-entrainers based on both tall oil and rosin. Bentz (2006a) and Esping and Löfgren (2006) found that SRAs also increase the freezable water content of cement pastes cured under **saturated** conditions at early ages which may have negative implications for the early-age frost resistance of these materials. This could also be a consequence of coarsened pore structure as discussed above.

A solution to the negative effect of SRA on the early age properties like air-entraing and retardation of setting (e.g. Brooks et al., 2000) and lower early strength (e.g. Folliard and Berke, 1997) could be to use LWA saturated with SRA solution as a distributer when needed (after setting) as described by Bentz (2005a) in the FLAIR (Fine Lightweight Aggregates as Internal Reservoirs) concept. FLAIR is utilization of pre-wetted fine lightweight aggregates for the autogenous distribution of chemical admixtures in general to mortars and concretes, but according to Bentz (2005a) further research is needed to determine the applicability of FLAIR to other admixtures than SRA such as corrosion-inhibiting admixtures and admixtures for mitigating alkali-silica reaction, and the practicality of utilizing the technology at ready-mix plants and pre-casting facilities. FLAIR might be a concept to pursuit in COIN.

Masanaga et al. (2007) developed a new SRA based on increased contact angle between pore water and the pore wall (θ in Eq. 4) since it adsorbs on the hydration products and contain a hydrophilic group. Their test on mortar with w/c = 0.44 showed a shrinkage strain of $390\cdot10^{-6}$ for only 0.3 % dosage of the new SRA vs. $380\text{-}405\cdot10^{-6}$ for 2% addition of the conventional SRAs. Another benefit was that the new SRA enabled air entraining for resistance towards freezing and thawing, unlike the traditional SRAs.

Bentz (2005a) tested a control mix and a mix with LWA and shrinkage reducing agent (SRA) either added to the mixing water or added as a 10 % solution in the LWA according to the FLAIR principle as outlined in Table 1. There was no effect on measured strain by the two SRA addition methods as seen from Fig. 9, but both methods reduced it relative to the reference. Unfortunately LWA saturated with SRA solution was not compared to LWA saturated with plain water. Thus, the question remains; if LWA saturated with pure water is sufficient or if there is an extra benefit in combining it with SRA.

4.2 Expanding cements and additives

4.2.1 General

A normal Portland cement concrete expands slightly during moist curing, but this effect is outweighed by the drying shrinkage that occurs on subsequent exposure to an atmosphere of normal humidity. If the concrete is restrained, the resulting tensile stress may be sufficient to crack it. In expansive cement, the expansion is increased, so as to balance or outweigh the subsequent contraction. Expansive cements, which were first described by Lossier (1936), may be categorized as shrinkage compensated or self-stressing cements. Thus, expansive cements and additives are a much more established technology than SRAs. Taylor (1998) gives a comprehensive review of such cements, of which some is repeated here. Nagataki and Gomi (1998) published a condensed review of expansive additives, mainly based on Ettringite formation, and with focus on Japanese experience.

Table 3 Mortar mixture proportions used in FLAIR study by Bentz (2005a)

Material	Mixture 1 CONTROL	Mixture 2 FLAIR	Mixture 3 CONVENTIONAL
w_O/c^A	0.30	0.30	0.30
Cement	1250 g	1250 g	1250 g
Water	365.4	365.4	359.01
Water-reducing admixture	16.0	16.0	16.0
Shrinkage-reducing admixture (SRA)	---	---	6.39
F95 (fine) sand	593.75	593.75	593.75
Graded sand (C778)	451.25	451.25	451.25
20-30 sand (C778)	451.25	451.25	451.25
S15 (coarse) sand	878.75	279.65	279.65
Prewetted fine LWA containing:	---	383.33	383.33
Water for LWA	---	---	63.89
10% SRA solution for LWA	---	63.89	----

$^A w_O/c$ calculated assuming 60 % water content for the water-reducing admixture and considering any SRA added to the mixing water as replacing an equal mass of water.

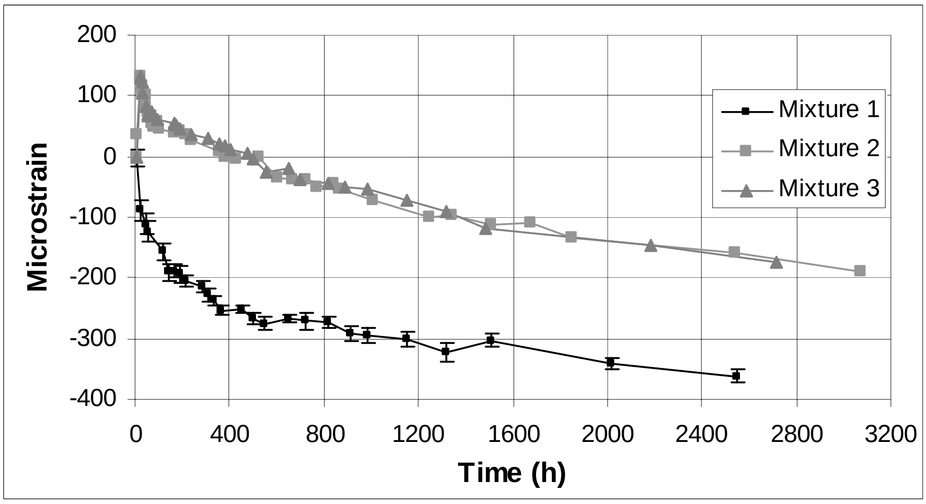

Fig. 9 Measured (average of two samples) autogenous deformations vs. time for the three mortar mixtures in the FLAIR study by Bentz (2005a). Error bars on lower curve indicate range of values for the two mixture 1 specimens.

In shrinkage-compensated cement, the object is to balance the drying shrinkage to prevent cracking. In practice, the expansion is restrained by reinforcement and a small compressive stress of 0.2-0.7 MPa is created in the concrete, which should preferably remain under slight compression after the normal drying shrinkage has occurred. Practical uses of shrinkage-compensated cements have included such structures as multi storey car parks or water storage tanks, in which it is desirable or essential to eliminate water leaks.

In self-stressing cement, a larger expansion is produced, with the object of achieving greater stresses in the reinforcement and the concrete to permit the production of thin, strong articles or structures, as in mechanical pre-stressing. Estimates of the maximum stress that can be safely achieved have ranged from 3.5 MPa (M 112) to 8 MPa (W36). Because the concrete expands triaxially, careful design and choice of curing conditions, including if necessary triaxial restraint, are essential. Self-stressing cements have been used both in the manufacture of precast pipes and other units and for in situ applications.

In any expansive cement, the amount of expansion and the period during which the expansive reaction occurs are critical. The reaction must take place after the concrete has developed some strength, but before exposure to reduced RH that will place it in tension, which could cause irreversible damage.

4.2.2 Expansive cements and minerals

Probably a majority of practical expansive cements have depended on the modification of a Portland cement in such a way as to increase the formation of Ettringite. Single expansive cement clinkers can be made, but it has been more usual to produce admixtures that are blended or interground with a normal Portland cement or clinker. Blending has the advantage that the fineness of the expansive admixture can be optimized, usually by grinding it less (i.e. leaving it more coarse) so as to delay the expansive reaction until the cement has developed the necessary strength. It also allows a single admixture to be used in differing proportions to make both shrinkage-compensated and self-stressing cements.

In a widely used US terminology, expansive cements based on Portland cement and calcium sulfate are categorized as types K, M or S, according to the source of the additional $A1_2O_3$ that is required. Type K cements, developed by Klein and Troxell (1958), contain $C_4A_3\bar{S}$ as an essential ingredient. They are usually produced by intergrinding or blending an ordinary Portland cement clinker with additional gypsum or anhydrite and an expansive clinker containing $C_4A_3\bar{S}$. The composition of the expansive clinker can be varied considerably in order to utilize the raw materials that are most economically available. Clinkers made in the USA contain for instance typically 8-50 % of $C_4A_3\bar{S}$ together with some anhydrite and usually some free lime (Mehta and Polivka, 1980). The proportions of expansive clinker and of gypsum or anhydrite or both that are added to the Portland cement depend on the composition of the expansive clinker and the degree of expansion required. Mehta and Polivka (1980) found that Type K shrinkage compensated cements made with Portland cement clinkers of low or moderate potential C_3A content and containing 6 % or more of SO_3 resisted chemical attack by sulfates, but that Types M and S cements did not.

Type M cements contain Portland cement, a calcium aluminate cement (CAC) and additional calcium sulfate. They were extensively studied in the former USSR. Mikhailov (1962) described self-stressing cement composed of Portland cement, CAC and gypsum typically in the proportions 66:20:14 that was used to produce precast units. Initial curing in air followed by hot water allowed strength development without formation of Ettringite, which occurred during a subsequent cure in cold water. Mixtures using alumina slag as the source of additional $A1_2O_3$ were also used, and only required curing in air followed by cold water (Mehta and Polivka, 1980, and Mikhailov, 1973). Mixtures of CAC with gypsum (Xue et al., 1986) or with gypsum and C_4AH_{13}, the latter made from CAC and lime (Mikhailov, 1962), have also been employed.

Type S cements are Portland cements high in C_3A and with suitable contents of calcium sulfate; they have found little favor as they are too difficult to control. The $A1_2O_3$ has also been supplied in forms other than those mentioned above. Impure alunite ($KAl_3(SO_4)_2(OH)_6$), which occurs as a natural rock, has been used, either after calcination (Volkov et al., 1976) or uncalcined (Wu and Wang, 1980). In the latter case it was mixed with Portland cement clinker, anhydrite and fly ash or slag and was found to dissolve relatively slowly, thus suitably delaying the expansive reaction.

The possibilities of using free lime or Periclase as expansive agents have also been investigated. Kawano et al. (1976) and Long (1983) described clinkers in which substantial proportions of free lime are present as inclusions in alite. In both cases, the raw mix included anhydrite. Long (1983) investigated and described the processes by which this microstructure was formed.

In type K cement, the expansion mechanism is the formation of Ettringite from $C_4A_3\bar{S}$ as may be represented by the equation

$$C_4A_3\bar{S} + 8\ C\bar{S}H_2 + 6\ CH + 74\ H_2O \rightarrow 3\ C_6A\bar{S}_3H_{32} \qquad [8]$$

Consideration of the relevant densities shows that the solid volume is approximately doubled by the reaction, and it has sometimes been assumed that this is sufficient to explain the occurring expansion. However, as the case of the normal hydration of Portland cement shows, a doubling of the solid volume does not necessarily cause significant expansion. The change in porosity must be considered, and depends on the extent to which the particles of the product are accommodated in the existing pore structure. Any adequate theory of the mechanism of an expansive reaction must be based on an understanding of the microstructure.

Odler and Jawed (1991) reviewed expansive reactions in concrete, including those produced through the use of expansive cements. Probably a majority of workers have accepted the view of Lafuma (1929) that expansion results from forces exerted by the growth of the Ettringite crystals. Of other theories, the most significant in relation to type K cements is that proposed by Mehta (1973), who attributed it to attraction of water molecules to Ettringite crystals of colloidal dimensions.

Bentur and Ish-Shalom (1974 and 1975) and Ish-Shalom and Bentur (1974 and 1975) studied mixtures of $C_4A_3\bar{S}$, CS and CH in pastes, alone or mixed with C_3S. Expansion did not begin until a certain critical degree of reaction, which was about 50 % at 20°C, had been reached. Using scanning electron microscope (SEM), light microscopy and mercury intrusion porosimetry, they confirmed earlier observations that the Ettringite was formed as porous coatings around the grains of $C_4A_3\bar{S}$, which were thus effectively caused to expand; expansion began when the expanding particles came into contact and exerted pressure on each other. In the absence of restraint, these particles could be treated as spheres, but under restraint they expanded in the directions in which the restraining forces were least. Essentially the same mechanism was described by Ogawa and Roy (1981, 1982a and 1982b), who found that Ettringite was formed initially as very small, unoriented crystals. After the degree of reaction (defined by the quantity of Ettringite formed) had reached about 50 %, Ettringite developed as radial growths of longer crystals. Contact between the Ettringite layers surrounding the $C_4A_3\bar{S}$ particles, and the associated expansion, began only after this stage had been reached. The change in Ettringite morphology was considered to be an important first step in causing expansion.

One study on type K cements showed no significant dependence of Ettringite crystal size on the Ca^{2+} concentration in the solution (Kurdowski and Thiel, 1981). In contrast, other investigators have found that suspensions of $C_4A_3\bar{S}$, $C\bar{S}$ and CH at high CaO concentrations produce

Ettringite in the form of a fine-grained coating on the $C_4A_3\bar{S}$ particles, but that in the absence of CH the ettringite forms long, thin needles (Mehta, 1973, Nakamura et al., 1969, and Okushima et al., 1969). In pastes containing $C_4A_3\bar{S}$, expansion occurs if CH is present but not if it is absent, even though ettringite is still formed (Nakamura et al., 1969, and Okushima et al., 1969).

The effect of CH in favoring expansion is explained on Mehta's theory by the decreased crystal size of the ettringite (Mehta, 1973). On the crystal growth hypothesis, the CH effect is explained by the differing microstructural location in which the ettringite is formed (Nakamura et al., 1969, and Okushima et al., 1969). If the CaO concentration in the solution is high, $Al(OH)_4^-$ ions cannot migrate far from the surface of the $C_4A_3\bar{S}$, and the ettringite is precipitated on the surface of that phase. Very high degrees of supersaturation may be reached locally at that surface, and, since the pressure that can be exerted by a growing crystal increases with the degree of supersaturation, strong expansive forces can be produced. The stresses may be further increased by the fact that ettringite formation is concentrated to relatively few places. The crystals are small due to the high degree of supersaturation. If the Ca concentration is lower, $Al(OH)_4^-$ ions can migrate more freely and the ettringite is precipitated more evenly throughout the material. The lower degree of supersaturation would also explain the increased size of the crystals.

The balance of the evidence favors the hypothesis that expansion in type K cements is caused by crystal growth. It is difficult to see why Ettringite crystals of the size (≈1µm in longest dimension) postulated by Mehta (1973) should attract water more strongly than C-S-H gel, which has a much higher specific surface area.

Apih et al. (2001) studied the hydration of portland cement with an expanding agent forming Ettringite, as well as the strength and water tightness of the product. A significant difference in hydration kinetics of modified versus non-modified cement was observed. The compressive strength of the modified cement was 70 % higher than the non-modified reference, while the water permeability became 60 % smaller.

Konik et al. (2007) produced an expansive agent by burning calcareous raw material and desulphurization gypsum (from cleaning of flue gases). The additive formulation was a calcium-sulphate component with aluminate clinker containing 60 % Al_2O_3. A 7 % addition to a CEM I cement resulted in a material with less shrinkage, while a 12 % addition gave an expansive binder.

Chandler et al. (2000) and Merchant et al. (2001) studied toughening cement-based materials through the control of interfacial bonding between aggregate and paste using type K expansive cement. The bond between aggregate and matrix was found not only to control the crack path but consequently the apparent toughness. Thomas and Jennings (2003) gave a mathematical relationship between the degree of restraint in a composite and the relationship between bulk volume change and pore volume change. Their observations provide guidelines for interpreting the meaning of gaps that often form between aggregate and paste in concrete.

Fu et al. (1995a and 1995b) studied a combination of pre-hydrated high alumina cement and gypsum as an expansive agent formulation producing Ettringite, which seemed to function well and could be regulated with a number of admixtures (Fu et al., 1995a).

Kaprielov et al. (2006) recently published a multi-component modifier for shrinkage - compensated and self-stressed high strength concrete based on a blend of Silica fume, fly ash, expansive agent and super-plasticizer in dosage s of 10-12 % of cement mass. The expansive agent was apparently a mixture of metakaoline and gypsum. It is thus likely that they utilized a similar principle as proposed in COIN for calcium carboaluminate hydrate; namely that the calcium aluminate hydrates from the pozzolanic reaction of metakaoline react further with gypsum to produce Ettringite.

Rongbing and Jian (2005) compared the performance of an Ettringite forming expanding additive (EA) to the performance of an SRA with respect to free drying shrinkage during 60 % RH and 20°C. The sample with EA shrunk actually 11.5 % *more* than the plain mortar wile specimens with SRA shrunk 26.5-37.7 % *less* than the plain mortar, depending on dosage. They concluded that this kind of EA must be combined with water curing to form the Ettringite, while SRA function well under dry conditions.

The expansion mechanism of lime (CaO) and Periclase (MgO) is simply the formation of their respective hydroxides in reaction with water forming expanding particles;

$$CaO\ (s) + H_2O = Ca(OH)_2\ (s) \qquad [9]$$

$$MgO\ (s) + H_2O = Mg(OH)_2\ (s) \qquad [10]$$

The rates of reaction in Eqs. 9 and 10 depend on particle size, calcining temperature in making them, hydration temperature, alkalinity of the pore solution and accessible water. The use of hard-burnt lime as expansive agent was studied by Deng et al. (1995), and it was pointed out that the hydroxyl ions in the pore water was important for the reaction in Eq. 9. Xu and Deng (2005) studied the use of calcined dolomite, $MgCa(CO_3)_2$, as a source of MgO based expansive agent in line with Eq. 10. To avoid CaO from the calcination, which would expand too early, they combined dolomite with silicate bearing minerals transforming it to C_2S instead.

Lilkov (1999a and 1999b) made lightweight cement products using cenospheres as light weight aggregate and an expansive agent based on hydroxide formation (i.e. Eqs. 9 and/or 10). The expansive additive helped overcome the drying shrinkage and strengthened the bond to bonding surfaces.

Schwartzentruber et al. (2004) compared the effect of the expansive additive CaO with that of different fibres in a test rig giving a crack risk indicator. While fibres increase the tensile strength, the expansive agent reduces restrained tensile stress. Their results are given in Table 4, showing that the expansive agent yielded the best result.

Table 4 Cracking risk for different additives in decreasing order (Schwartzentruber et al., 2004).

Additive	Dosage	Crack risk indicator (%)
PVA fibre	1 vol%	66
Reference	-	58
Glass fibre	1 vol%	57
Brassed metallic fibre	1 vol%	54
Galvanised metallic fibre	1 vol%	53
Expansive agent (CaO)	1% of cement mass	33
Brassed metallic fibre	2 vol%	32
Galvanised metallic fibre	2 vol%	26
Expansive agent (CaO)	3% of cement mass	-6

Toutanji (1999) made a repair mortar based on silica fume, polypropylene fibres and expansive cement. He found that 5 % silica fume combined with 0.3 vol% fibre resulted in optimum mix design for repair applications from the standpoint of workability, bond, strength, length change and permeability.

4.2.3 Gas forming additives

According to Mailvaganam (1984), gas forming admixtures are meant to control settlement and provide expansion in the plastic stage, while calcium sulphoaluminate and lime based expansive agents (section 4.2.1) are controlling settlement and provide expansion in both plastic and hardened state. The materials that release hydrogen gas is magnesium (Mg), aluminium (Al), silicon (Si) and zinc (Zn), although aluminium is by far the most common;

$$2\ Al\ (s) + 6\ H_2O = 2\ Al(OH)_3\ (s) + 3\ H_2\ (g) \qquad [11]$$

Note that reaction 11 is catalysed by the hydroxides in the pore water and will not proceed in pure water.

Mailvaganam (1984) lists the following applications of gas forming admixtures in concrete, mortar and grout;

- Improvement of the bond of steel to concrete of horizontal reinforcing rebar in deep beams
- Improvement of the effectiveness of grouts by off-setting volume changes due to shrinkage and settlement in the bedding of machinery and under-pinning applications
- Filling of water-tight joints and grouting of cracks in repair work
- Void filling applications, such as pre-packed aggregate concrete and prestressed concrete ducts
- Improvement of the homogeneity of concrete
- Production of cellular and self-stressed concrete
- Oil well cementing of porous rock formations
- In cement-based water-proofing coatings

Gas forming additives will not be elaborated further in this report since the expansion is more difficult to control in time and amount compared to Ettringite based expansive agents, and not to forget shrinkage reducing admixtures (SRAs) that can not produce over-expansion but only mitigate shrinkage stresses.

4.3 Blends of shrinkage reducing admixtures and expanding additives

There are a few papers on the combination of SRA and expanding lime.

Collepardi et al. (2005) claimed a synergy between the SRA neopentil glycol, $(CH_2)_2$-C-$(CH_2OH)_2$, and lime since the combination of the two was better than the sum of effects when used separately. This was manifested as more effective expansion in absence of wet curing as well as lower shrinkage after removal of the polyethylene sheet used to simulate the protection from drying before the demolding at the job site. Collepardi et al. (2005) claimed that this synergy does not exist when an expansive agent forming Ettringite is used.

Maltese et al. (2005) shed light on the mechanism for the above synergy, by showing pictures (Figs. 10-12) indicating that the SRA changes the morphology of the calcium hydroxide produced from lime to be more elongated prismatic, rather than hexagonal plates. They also showed that there was less calcium hydroxide produced when SRA was combined with CaO then for CaO alone, pointing at the possible formation of a compound between the two rather than just a morphology change. This is not far fetched as we know that the analytical method for determination of free lime in cement involves extraction of lime with glycol.

Fig. 10 ESEM (Environmental Scanning Electron Microscope) micrograph of paste with 3 % CaO after 2 h of curing.

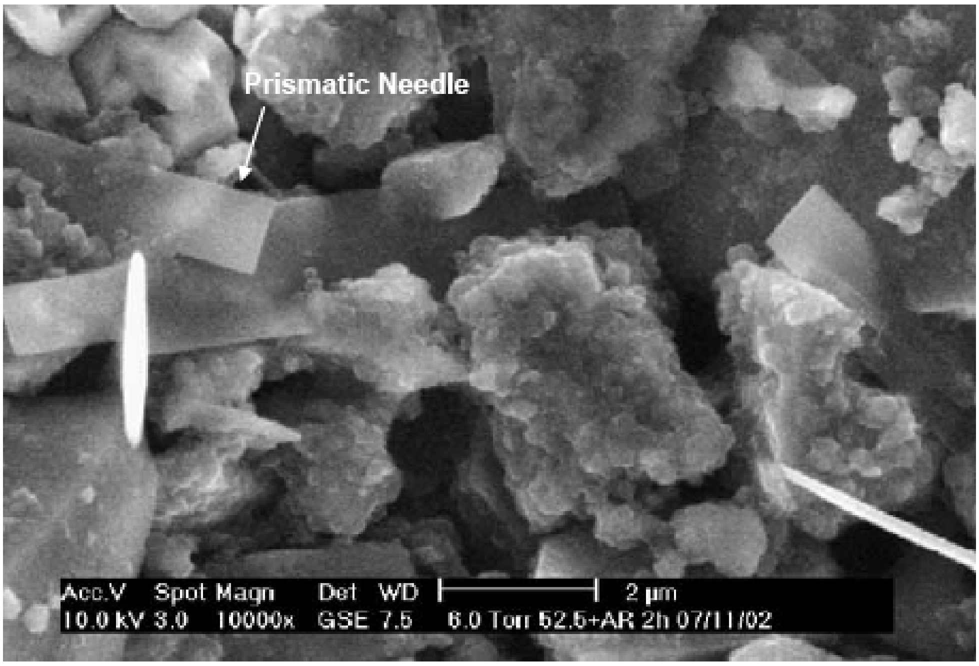

Fig. 11 ESEM micrograph of paste with 3 % SRA after 2 h of curing.

The possible formation of a chemical compound between glycol based SRA and calcium hydroxide, even when calcium hydroxide is produced from cement hydration alone (Fig. 11) and not CaO, is yet another potential mechanism of how SRAs may function.

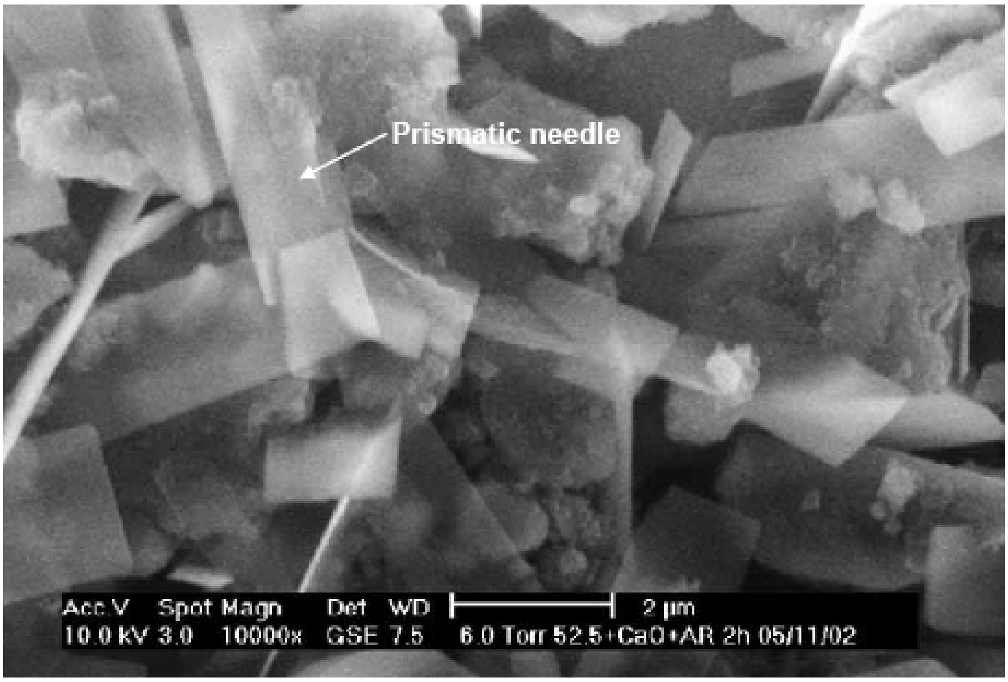

Fig. 12 ESEM micrograph of paste with 3 % CaO and 3 % SRA after 2 h of curing.

Recently, Collepardi et al. (2006) took this synergy further by using a combination of a polyacrylate based superplasticizer containing shrinkage reducing agent groups (PA/SRA) with lime as expanding agent. Collepardi et al. (2006) claimed that an outside floor slab was cast with up to 6 m contraction joints and without wet curing using PA/SRA alone. No cracks were observed 8 months after casting. By combining this PA/SRA with CaO they made a shrinkage-compensating concrete whose restrained expansion did not need any wet curing. With this they cast an 800 m^2 concrete floor without contraction joints, but contraction joints were made at the end of the day. No cracks were recorded 4 months after casting. Collepardi et al. (2006) concluded that the key-point of this joint-less floor is the robustness and crack-free performance that can be obtained even in the absence of wet curing. The PA/SRA may be similar to the type discussed by Nakanishi et al. (2003).

5 FUTURE RESEARCH

The mitigation of autogenous shrinkage cracks by saturated, surface dry LWA is well proven, but the potential of saturating the LWA with solutions of admixtures that otherwise would have interfered with the initial setting and hardening has not yet been fully exploited. The obvious saturation admixture would be a solution of a shrinkage reducing admixture (SRA) to see if this would give something extra over plain water.

It is recommended that the apparent synergy of SRAs with the expanding additive CaO is further studied to see if this can be an economical and efficient solution to joint- and crack-free concrete slabs in practice.

6 CONCLUSION

This report presents a literature review on mitigation of autogenous and drying shrinkage cracking by shrinkage reducing agents (SRAs) as well as expansive additives.

The SRAs are often propylene glycol derivatives believed to function by lowering the surface tension of water and thereby the tensile stresses, but the mechanism is disputed.

Expansive agents are usually formulations that produce Ettringite, but reports are also found on hydroxide forming compound like lime (CaO) and Periclase (MgO).

There seems to be an interesting synergy in combinations of glycol based SRA and CaO expanding agent, which should be further investigated for practical applications within COIN.

A third class of expanding additives is gas forming admixtures, in particular aluminium powder generating hydrogen gas. However, these seem more difficult to control in terms of timing and expansion.

Fine LWA saturated with solutions of admixtures (e.g. shrinkage reducing admixture) that otherwise would interfere with the initial setting and hardening of cement has not yet been fully exploited and is also recommended for pursuit in COIN.

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