

# Self-desiccation and self-desiccation shrinkage of silica fume-cement pastes

LV Yang<sup>1, a \*</sup>, YE Guang<sup>1, 2, b</sup> and DE SCHUTTER Geert<sup>1, c</sup>

<sup>1</sup>Magnel Laboratory for Concrete Research, Department of Structural Engineering, Ghent University, 9052 Ghent, Belgium

<sup>2</sup>Microlab, Faculty of Civil Engineering and Geosciences, Delft University of Technology, 2600 GA Delft, The Netherlands

<sup>a</sup>Yang.Lv@ugent.be, <sup>b</sup>G.Ye@tudelft.nl, <sup>c</sup>Geert.DeSchutter@ugent.be

\*corresponding author

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## Abstract.

Self-desiccation is one common phenomenon of high-performance cementitious materials, which are characterized by low water/binder (w/b) ratio and high mineral admixture incorporation. As a consequence, large magnitude of self-desiccation shrinkage, a key factor which influences the cracking behavior of concrete, develops rapidly in the cement matrix due to the internal relative humidity (RH) decrease and capillary pressure induced by self-desiccation.

The objective of this study is to evaluate the behavior of self-desiccation and self-desiccation shrinkage in silica fume (SF) blended cement pastes with low w/b ratio of 0.25. The self-desiccation process was revealed by the measurement of internal RH of the sealed cement pastes with conventional method of hygrometer. The shrinkage of the sealed cement pastes was measured by the corrugated tube method, permitting measurements to start at early age.

Experimental results revealed that SF blending leads to a higher internal RH, indicating slower self-desiccation process, compared with pure cement paste. Consequently, less self-desiccation shrinkage was observed in SF blended cement pastes than that in pure cement paste.

## Introduction

(Ultra-) High performance concrete (HPC/UHPC) has become popular due to its excellent mechanical and durability properties. In order to satisfy the required performance of HPC/UHPC, low w/b (water/binder) ratio with high quantity of binder is essential. Moreover, different kinds of cement replacement materials, such as silica fume (SF), are usually added to them because a low porosity and permeability are desirable. In particular, a lower w/b ratio and high binder content with the presence of certain supplementary cementitious materials (SCMs) can cause a significant drop in the internal relative humidity (RH) in the cement paste during sealed hydration [1]. It is the so-called self-desiccation, and will result in large magnitude of self-desiccation shrinkage which, if restrained, could increase the risk of early age cracking of concrete, resulting in a decrease in durability and long-term performance [2].

With the further application of HPC/UHPC, self-desiccation and self-desiccation shrinkage have drawn growing interest of research. Based on definitions from physical chemistry, Jensen and Hansen [3] proposed the following terminology.

Autogenous relative humidity change:

The change of internal relative humidity in a closed, isothermal, cementitious material system not subjected to external forces.

Self-desiccation:

Autogenous relative humidity change of a set cementitious material system caused by chemical shrinkage.

Self-desiccation shrinkage:

Autogenous deformation of a set cementitious material system caused by chemical shrinkage.

One of the key problems involved in the research is the determination of time-zero, i.e., the time for the start of self-desiccation shrinkage measurement. Accurate determination of the time-zero is critical for self-desiccation shrinkage measurement. In terms of cracking, shrinkage occurring before the time-zero is of little practical significance as it may have little practical consequence in residual tensile stress development. Conversely, measurement of shrinkage after the time-zero may substantially underestimate the actual shrinkage [4]. The lack of uniform standard about the time-zero causes great difficulty in comparing the results available in the existing literature [4]. Many time-zero criteria have been suggested in the literature [5], among which final setting time is generally accepted as the time-zero.

In order to determine the time-zero accurately, it is necessary to have a clear understanding of the mechanisms behind the phenomena mentioned above. Based on the schematic illustration of self-desiccation and self-desiccation shrinkage proposed by Jensen and Hansen [3], Lura et al. [6] present an evaluation of basic mechanisms behind those phenomena and found that there is a very close relation between the internal RH change and self-desiccation shrinkage. Once the hydrates percolate and the first solid paths are formed in the hardening paste, indicating the start of development of a solid skeleton, the paste gains gradually increased rigidity and starts to resist further volume decrease caused by chemical shrinkage. It results in air voids developing within capillary pores and menisci formation at the pore solution-vapour interfaces, leading to the internal RH drops (Kelvin's law), i.e., self-desiccation. The radius of the menisci progressively decreases as the largest pores empty and the porosity fills up with hydration products. At the same time, the capillary pores are progressively emptied by chemical shrinkage, which is accompanied by a continuous decrease of the internal RH. The increasing curvature of the menisci leads to the development of hydrostatic tensile stresses in the pore solution and compressive stresses exerted on the solid skeleton (Laplace's law), which lead to the bulk deformation of the cement paste, i.e., self-desiccation shrinkage [3,6].

As defined in the terminology [3], the term "set" refers to as solid skeleton formation. Although the solidification as well as the concurrent stiffening develops very slowly, making the precise onset of these processes practically impossible, the precise internal RH measurements of the cement pastes, starting from the pastes being still in fluid phase, could supply reasonable experimental data to discuss the self-desiccation process and time-zero of self-desiccation shrinkage caused by self-desiccation [7]. Based on the precise measurements of RH and early age shrinkage on the sealed samples, the effect of silica fume (SF) blending on the self-desiccation and self-desiccation shrinkage in the cement pastes with low water to binder (w/b) ratio was studied in this study.

## Experimental study

**Materials.** Ordinary Portland Cement (OPC) CEM I 52.5 N and undensified 920U silica fume (SF) from Elkem was used in this study. The chemical composition of each material was analyzed by means of X-ray fluorescence (XRF) technique, and the results are shown in Table 1. Cement paste blended with or without 20% SF by weight with w/b ratio of 0.25 was prepared. A polycarboxylate-based superplasticizer (Glenium 51, Conc. 35% BASF) was used to modify the fluidity of cement pastes. The dosage of the superplasticizer was kept constant as 1.4 wt.% of binder, to limit its influence on the setting and hydration of cement.

Table 1 Chemical composition of Cement and SF (- not available)

Material	Chemical composition (% by weight)								
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	LOI
Cement	63.12	18.73	4.94	3.99	3.07	0.41	0.77	1.02	2.12
SF	0.19	94.97	0.35	1.88	-	0.41	1.45	0.62	-

**Testing program.** The hydration heat flow of cement pastes blended with and without SF was measured by an isothermal calorimeter at 20 °C (Thermometric). About 15 g of freshly mixed pastes were poured into glass vials immediately after the mixing. The calorimetry results are normalized by gram of binder in the mixture.

Early age shrinkage of sealed curing cement paste was measured by modified corrugated tube method based on ASTM C1698 [8]. The fresh mixed cement paste was casted into the corrugated tubes of 420 mm  $\phi$  29 mm and vibrated. For each mixture, three specimens were prepared and placed in a dilatometer rig (immersed in a temperature-controlled glycol bath), which was equipped with linear variable differential transformers (LVDTs) with a measuring accuracy of 2.5  $\mu\text{m/m}$ . The autogenous shrinkage was automatically recorded every 10 min, starting from about 30 min after mixing until 7 d.

Final setting of cement paste was determined using the Vicat needle test according to ASTM C 191 [9].

The internal equilibrium relative humidity (RH) of hydrating cement paste was measured on two independent sealed paste specimens by the Rotronic hygroscope station, which is equipped with a Pt-100 temperature sensor and a DMS-100 H relative humidity sensor. During the measurement, the stations were immersed in water bath to maintain the temperature of the sample and the sensor at  $20 \pm 0.1$  °C. The sensors were calibrated before measurement with standard salt solutions with known RH in the range 65-95% at 20 °C, giving a measurement accuracy of  $\pm 0.5$  % in the absolute RH. More detailed information about the internal RH measurement can be found in the study [7]. The data were logged every 3 min automatically, and the measurement was continued until the age of 7 d.

## Results and Discussion

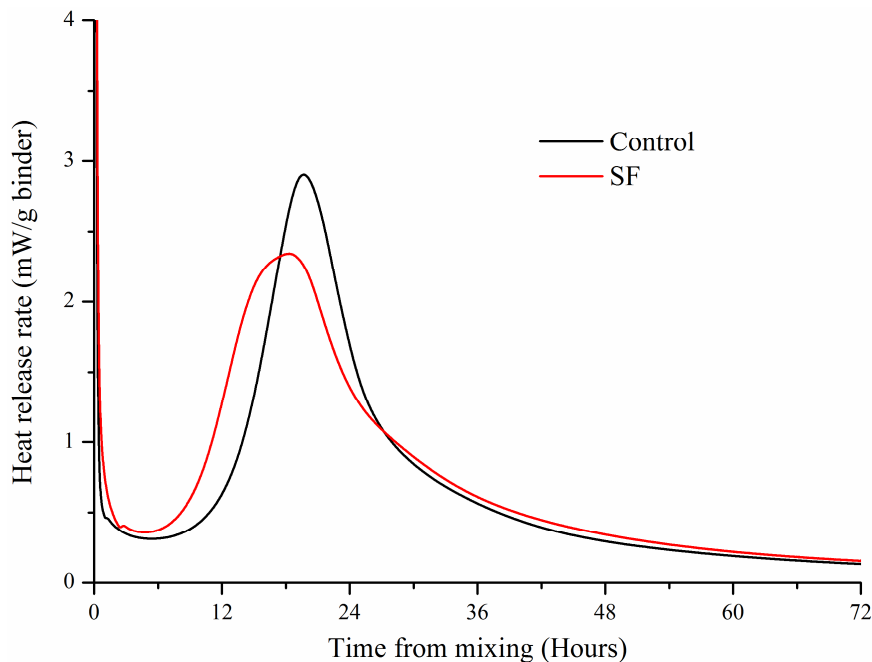


Fig. 1. Evolution of hydration heat of cement paste (20 °C)

**Evolution of hydration and free shrinkage.** It is known that silica fume shows an acceleration effect on the cement hydration, as the amorphous nature and very fine particle of silica fume make it highly reactive. Silica fume experiences rapid dissolution in the pore solution with the presence of  $\text{Ca}^{2+}$  and  $\text{OH}^-$  and a supersaturation of silica with respect to a unstable silica-rich phase, which will form a layer on the surface of the silica fume particles. The layer is then partly dissolved and the remainder acts as a substitute on which conventional C-S-H is formed [10]. This leads to rapid dissolution of cement particles and accelerated hydration, which can be observed in the hydration heat evolution curves of the cement pastes as shown in Fig.1. The SF sample showed a shorter dormant period and it reached its main maximum heat release rate earlier than that of control paste. The

reduced maximum heat release rate of SF sample is due to the dilution effect as 20% of cement by weight was replaced by SF.

With the hydration going on, the cement paste undergoes volume reduction, i.e. the chemical shrinkage, due to the fact that the volume occupied by the hydration products is smaller than that of the reactants [1, 6]. During early age, cement based materials undergo three different phase stages [11] including liquid stage, skeleton formation stage and hardening stage. As long as the cement paste is fluid (liquid stage), the chemical shrinkage is totally converted into an external volume change.

The corrugated tube method used in this study permits shrinkage measurement to start at very early age. Fig. 2 shows the free shrinkage of cement pastes; the start time of measurement was 36 min and 40 min from mixing for control and SF sample, respectively. As shown in Fig. 2, both samples underwent quickly shrinkage at early age; SF sample showed higher shrinkage than that of control sample during the first 15 h after mixing. This is due to the acceleration effect of silica fume on the cement hydration.

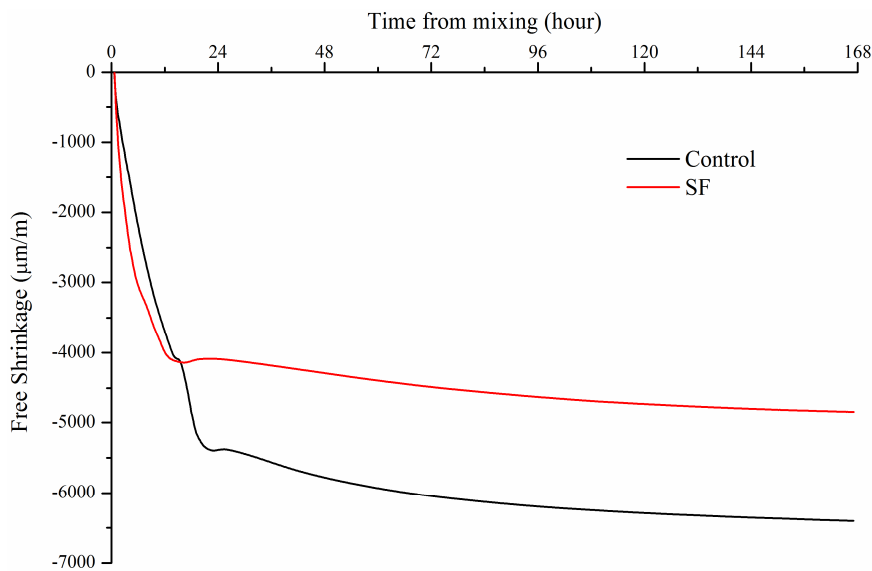


Fig. 2. Free shrinkage of cement paste

**Self-desiccation and self-desiccation shrinkage.** With the hydration reaction between cement and water going on, a skeleton will form as a result of the hydration products (skeleton formation stage). As discussed previously in Section Introduction, during this skeleton formation stage, the hydrates will percolate and the solid paths are formed in the hardening paste. As a result, the stiffness increases and gas bubbles start to nucleate and grow in the bigger pores, giving rise to the formation of water-air menisci accompanied by a continuous decrease of the internal RH (self-desiccation). The presence of menisci causes tensile stresses in the pore fluid (Laplace's law) and compressive stresses exerted on the solid skeleton, leading to the bulk deformation of the cement paste, called the self-desiccation shrinkage [6]. In some literature, it is called autogenous shrinkage [1, 3].

As the skeleton of the cementitious system becomes interconnected, the development of autogenous shrinkage and chemical shrinkage will begin to diverge. The divergence phenomenon of autogenous shrinkage from chemical shrinkage has been observed by several researchers [12-14] who performed simultaneous volumetric tests of chemical shrinkage and autogenous shrinkage on cement pastes. The divergence time, the point Barcelo et al. [12] refer to as "suspension-solid transition", is the time-zero at which the self-supporting skeleton starts to develop and the stresses begin to develop. However, the process "suspension-solid transition" as well as solidification develops very slowly, making the precise onset of these processes practically impossible.

As final setting time is the most common criteria for determining the threshold within the suspension to solid transition, it is more widely accepted as the time-zero, the start time for the autogenous shrinkage measurement [8]. Note that the final setting determined by Vicat needle test is highly scattered, which will result in a large influence on the absolute value of shrinkage as the rate of shrinkage is generally high around final setting time (can be seen in Fig. 3). Moreover, shrinkage

occurring around setting time is of lower importance in terms of the cracking risk. The high compliance of the material at this stage can lead to pronounced deformation even under very low forces, but at the same time this deformation is not expected to lead to the buildup of considerable self-induced stress [15].

Actually, as mentioned before, the self-desiccation shrinkage (or autogenous shrinkage according to some literature) is linked to the internal RH decrease. Although it is practically impossible to determine the precise onset of the slowly developed “suspension-solid transition” and solidification process, the precise internal RH measurements of the pastes, starting from the pastes being still in fluid phase, supply reasonable experimental data to discuss the time-zero of self-desiccation shrinkage caused by self-desiccation. A systematic research about determining the time-zero in low w/b ratio cement pastes was carried out by Huang and Ye [7], and they came to the conclusion that the time-zero could be linked to the time when internal RH begins to drop.

Fig. 3 displays the relation between the free shrinkage and the internal RH of the cement pastes as function of time from mixing. As shown in Fig. 3, the internal RH of control paste stabilized at around 98% till 20.8 h after mixing, and then it showed a monotonic decrease to 78.1% at 7 d after mixing. The time for the occurrence of self-desiccation (the time when internal RH starts to decrease) in SF blended paste is 15.8 h, earlier than that of control sample, indicating an earlier formation of solid skeleton in SF blended cement paste. This can be partially attributed to the acceleration effect of silica fume on the cement hydration. Furthermore, the presence of SF could lead to pore-size refinement in cement mixtures, as it basically acts as filler due to its fineness. SF particles themselves are also involved in forming more fine porous microstructures [16]. Although the self-desiccation in SF blended paste occurred earlier than that in control paste, higher internal RH (82.6%) at 7 d was observed in SF blended paste.

In this study, the internal RH measurements were started from approximately 4 h after mixing and onwards. The measured RH drop is mainly attributed to self-desiccation of the cement paste under sealed curing condition. But the initial RH drop due to dissolved salts in the pore fluid should also be taken into account. Consequently, the total RH can be approximated according to the following formula [17]:

$$RH = RH_s * RH_k \quad (1)$$

$RH_s$  is the initial RH drop due to dissolved salts in the pore fluid, which can be estimated according to Raoult's law [17].

$$RH_s = X_1 \quad (2)$$

where  $X_1$  is molar fraction of water in the pore fluid.

$RH_k$  is the RH drop due to the meniscus formation and the consequent self-desiccation, which can be calculated according to Kelvin's equation:

$$RH_k = \exp\left(-\frac{2\gamma M \cos \theta}{\rho r RT}\right) \quad (3)$$

where  $\gamma$  is surface tension of pore fluid,  $M$  is molar weight of pore fluid,  $\theta$  is contact angle between pore fluid and solids,  $\rho$  is density of pore fluid,  $r$  is radius of the meniscus,  $R$  is ideal gas constant (8.314 J/(mol·K)) and  $T$  is absolute temperature (in this paper, 293.15 K).

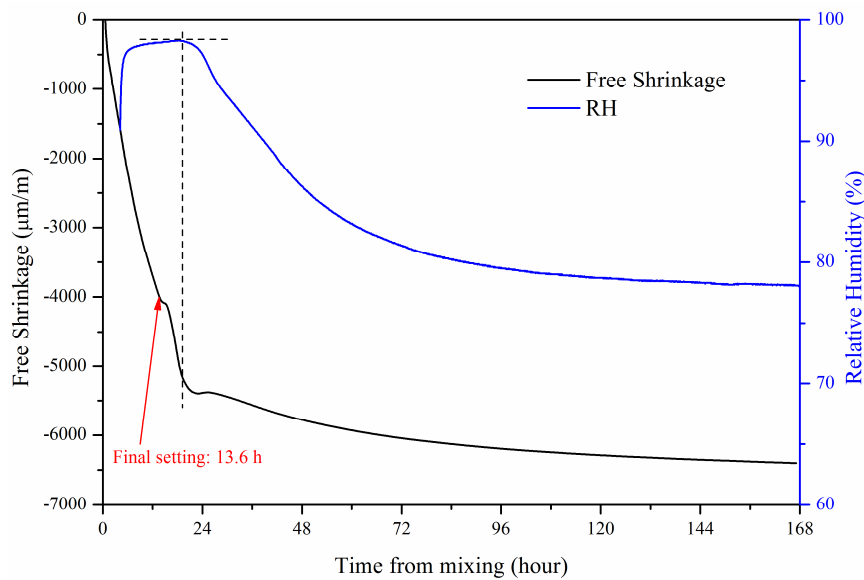
Then equation (1) could be:

$$RH = RH_s * RH_k = X_1 * \exp\left(-\frac{2\gamma M \cos \theta}{\rho r RT}\right) \quad (4)$$

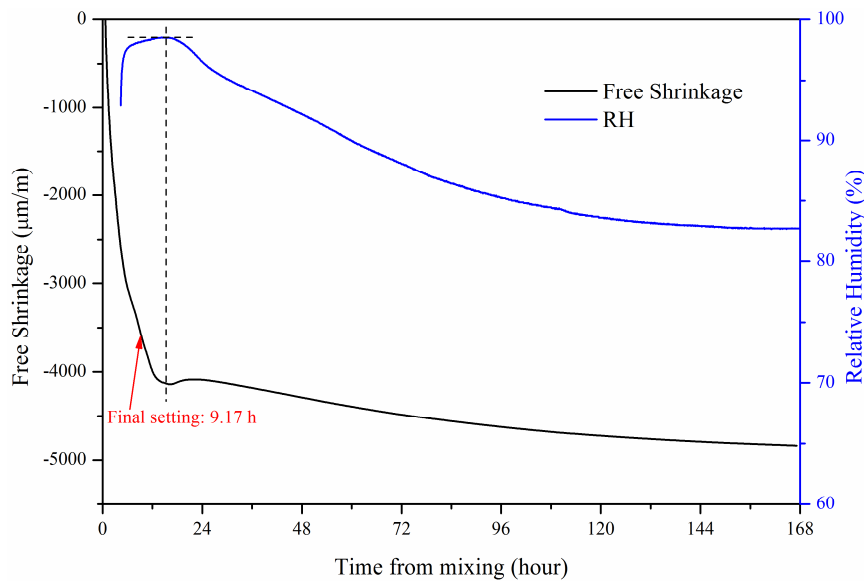
As shown in Fig. 3, the RH was stabilized at around 98% for both mixtures during early age, when the cement is fluid and the pore system is saturated. This is the initial RH drop due to the dissolved salts in pore solution.

Assuming that the initial RH drop measured in the first hours due to the dissolved salts remains constant during hydration, the RH drop due to self-desiccation for the cement paste is directly related to the  $r$ , the radius of the meniscus, i.e. the largest capillary pore filled with water in the cement paste system. So it has to be noted that, although the SF could refine the pore structure in the blended cement paste system, it does not certainly lead to lower internal RH and a quicker self-desiccation process. Anyway, further research is needed to explore why the SF blending shows a higher internal RH.

Furthermore, as shown in Fig. 3, no internal RH drop (self-desiccation) was observed at around the final setting time for each mixture, but the internal RH began to drop several hours after final setting time, corresponding to a knee point in the shrinkage curve, which is the so-called time-zero [7]. After the time-zero, both samples underwent a monotonic shrinkage at a much slower rate than that before the time-zero, corresponding to the decrease of the internal RH (self-desiccation).



(a) Control



(b) SF

Fig. 3. Relation between free shrinkage and RH of cement paste as function of time from mixing

According to the time-zero defined by the onset of self-desiccation, the self-desiccation shrinkage of each mixture is presented in Fig. 4. The control sample showed a self-desiccation shrinkage of 1098  $\mu\text{m/m}$  at 7 d after mixing. A reduced self-desiccation shrinkage was observed in the SF blended paste (700  $\mu\text{m/m}$ ) at 7 d, corresponding to the slower self-desiccation process (higher internal RH as shown in Fig. 3).

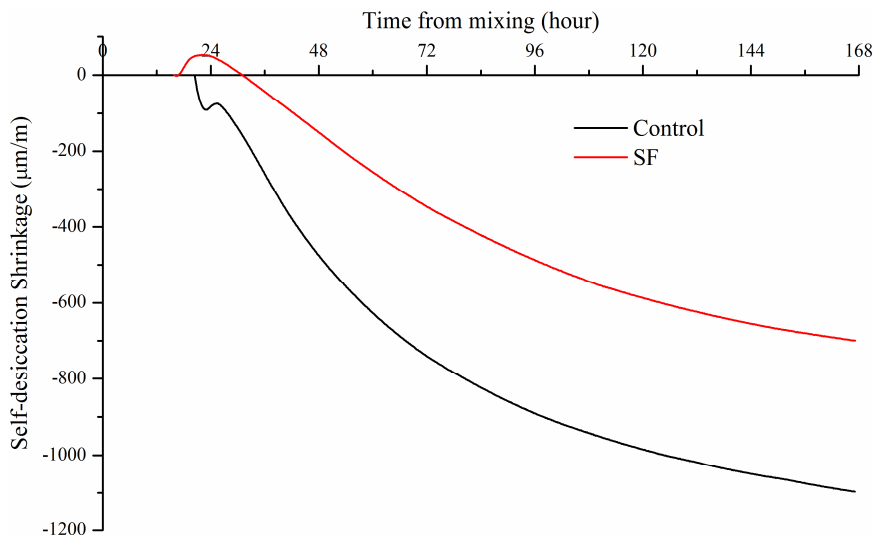


Fig. 4. Self-desiccation shrinkage of cement paste

## Summary

This paper studies the effect of SF blending on the self-desiccation and self-desiccation shrinkage in cement pasts with low w/b ratio of 0.25. No self-desiccation was observed at the final setting time for both mixtures; self-desiccation seems to occur several hours later than the final setting time, corresponding to a knee point in the shrinkage curves. This point, the time when internal RH begins to drop, was selected as the time-zero for self-desiccation shrinkage.

The cement paste blended with SF shows a higher internal RH than that of control sample during the 7 d after mixing, indicating a slower self-desiccation process. The reduced self-desiccation shrinkage in SF blended paste seems to be related to the slower self-desiccation.

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