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Controlling the coefficient of thermal expansion of cementitious materials – A new application for superabsorbent polymers

Mateusz Wyrzykowski [a,b,*], Pietro Lura [a,c]

[a] *Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*
[b] *Department of Building Physics and Building Materials, Technical University of Lodz, Poland*
[c] *Institute for Building Materials (IfB), ETH Zurich, Switzerland*

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ABSTRACT

Self-desiccation occurring in low w/c cement paste leads not only to autogenous shrinkage, but also causes an increase of the coefficient of thermal expansion (CTE) at early ages. This increase can reach about 70% or even more in the first days of hydration. The latter effect is due to the internal relative humidity (RH) changes induced by temperature changes, which cause additional deformation acting in the same direction as the pure thermal dilation in a partially saturated cementitious material. Internal curing by means of superabsorbent polymers (SAP) has recently been proven effective for promoting hydration of cement and for limiting self-desiccation and autogenous shrinkage. This study shows that SAP are also able to control or even completely eliminate another negative effect of self-desiccation, the increase of the CTE. This is to the authors' knowledge the first such application of SAP. In this work, both aspects of SAP use are investigated, with special focus on limiting the thermal expansion coefficient. First, self-desiccation and self-desiccation shrinkage and their reduction with SAP are investigated in cement pastes and mortars using water-activity measurements and linear shrinkage measurements with corrugated tubes. Next, the thermal expansion is studied experimentally using both volumetric and linear methods for a series of cement pastes and mortars of different w/c. Addition of SAP in cement pastes and mortars is proven to practically eliminate the increase of the CTE during the first days of hardening, limiting the CTE to only 60–70% of the value developed for materials without SAP addition. The reduction of the CTE is possible thanks to maintaining high internal RH levels and consequently reducing the temperature effect on RH.

1. Introduction

The increase of the temperature due to the exothermic nature of hydration, followed by non-uniform cooling to ambient temperature, will cause formation of temperature gradients in a concrete structure. These temperature gradients and resulting non-uniform thermal deformations within the element are responsible for the so-called self-restraint effect, which leads to the buildup of considerable thermal stresses. Moreover, the structure is usually restrained externally, e.g. by adjacent structural members. Finally, internal restraint exists since concrete components, i.e., aggregates, cement paste and optionally reinforcement, often reveal mismatch in thermal expansion. In consequence, if the thermal stresses exceed the tensile strength of the material, microcracks or even macroscopic cracking can be induced, Fig. 1, [1]. Thermal stresses and risk of cracking will depend on the characteristics of the structure (mainly size, degree of restraint) and properties of the material, among which the tendency of the material to deform due to the temperature change will play a paramount role. The latter quantity is referred to as the coefficient of thermal expansion (CTE), e.g. [2–6]. This term is commonly used in literature, even if it describes both the contraction and expansion potential of the material, which are generally found to be symmetrical for temperature steps encountered in practice. This approach is also used in the present work, where CTE refers to the linear strain due to the unit change of temperature in either direction. Bažant [7] suggested that the total thermal deformation in partially-saturated concrete origins from the following mechanisms: (1) pure thermal dilation of constituents, (2) thermal shrinkage or swelling (which is thought to be due to redistribution of water from gel to capillary pores, and resulting shrinkage with increasing temperature, or vice versa) and (3) RH changes due to the temperature changes, see also [3]. It needs to be underlined that the CTE accounts by definition for the immediate deformations and not for the delayed deformations that follow the mechanism (1) and that are inherent to mechanism (2). These delayed deformations are due to pressure

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* Corresponding author at: Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland.
E-mail address: mateusz.wyrzykowski@empa.ch (M. Wyrzykowski).

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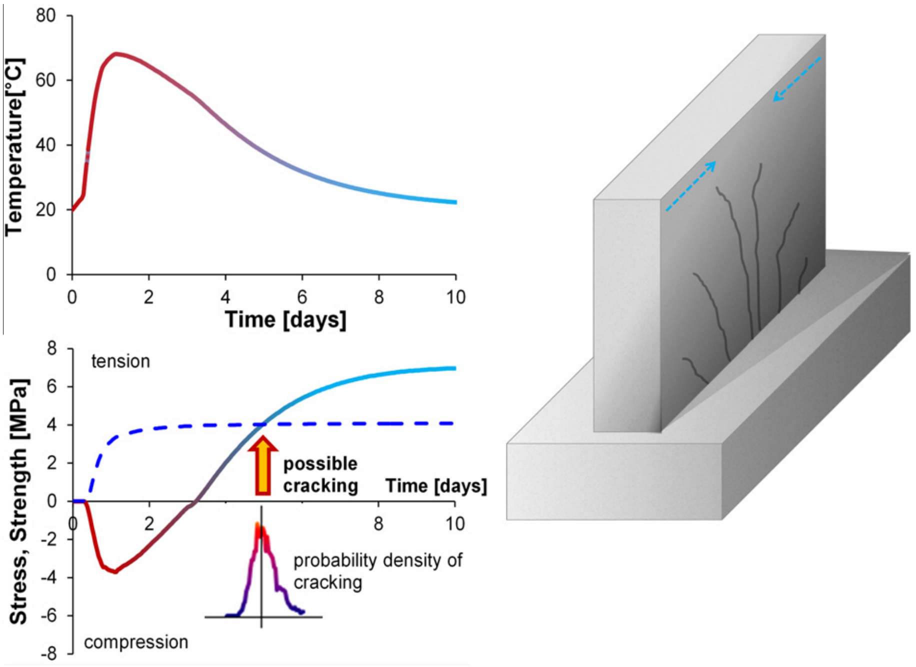

Fig. 1. Schematic illustration of thermal cracking problem in concrete. Temperature and stress/strength development data come from numerical simulations of self-heating in the center of a 1 m-thick concrete wall [1].

dissipation in pores (causing a delayed recovery of pure thermal dilation, see [6,8]), or due to long-term effect of the redistribution of water species [7], respectively. The mechanism (3) is thought to result in immediate deformation [3]. It needs to be however realized that the term *immediate* refers to the time spans ranging from minutes to hours needed to obtain in the sample thermal equilibrium and quasi-equilibrium of the corresponding thermal deformations. It should be however mentioned that the importance of delayed effects is expected to decrease with a decreasing saturation degree in the pores [3].

It has long been observed that the desaturation of pores in cementitious materials is accompanied by a considerable increase of the CTE [2–5,9]. This moisture dependence of the CTE has been shown [3,4,7] to be exclusively an effect of the mentioned RH dependence upon temperature (mechanism (3)). At the same time, after resaturating the material at later age, an almost complete recovery of the CTE back to the values measured at the initial stages after setting was reported in [3]. This fact suggests that hydration itself has a negligible net effect on the evolution of the CTE in the saturated state after setting and that the increase of the CTE can be exclusively attributed to the RH-temperature mechanism. This mechanism is usually quantified by means of the coefficient $\Delta RH/\Delta T$ [3,4,10], which expresses the change of RH due to the unit change of temperature, similarly as the CTE describes strains. In capillary porous media like concrete, the coefficient $\Delta RH/\Delta T$ takes positive values; hence an increase of temperature leads to an increase of RH in pores and the resulting additional deformation acts in the same direction as the pure thermal dilation, i.e., an additional expansion is induced by an increase of temperature. Furthermore, $\Delta RH/\Delta T$ increases as RH decreases for RH levels encountered during self-desiccation, Fig. 2. This is due to the increasing isosteric enthalpy of sorption with decreasing water content, for details see [3,10,11]. In low w/c cement pastes, the drop of RH due to self-desiccation only may lead to an increase of the CTE of even more than 2 times respect to the value at full saturation [3,9], while in high performance concrete (HPC) an increase by about 30% [5] or even 60% [3] was reported.

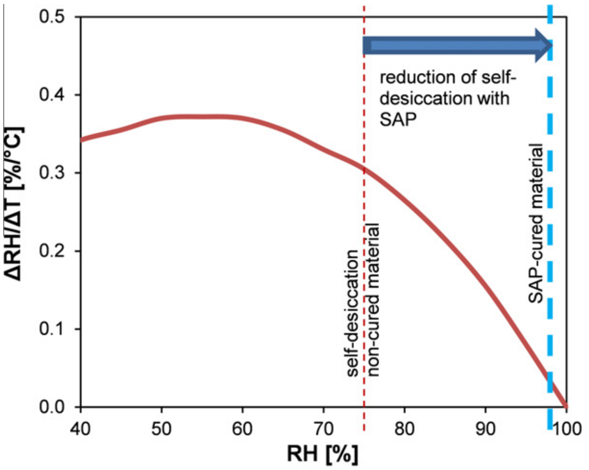

Fig. 2. Schematic representation of the concept for reducing CTE. The curve presents the $\Delta RH/\Delta T$ increase with decreasing RH and the reduction of this phenomenon with SAP (compare with Fig. 6 where the reduction of self-desiccation with SAP is presented). The curve comes from Radjy et al. [10] and is a fit to the experimental data of a w/c 0.50 cement paste equilibrated at different moisture contents and exposed to changing temperature with monitored corresponding changes of vapor pressure. Similar trends can be found in [4]. Note that the changes of CTE will follow the trend of the $\Delta RH/\Delta T$ coefficient, see [4]. Thus, reducing the $\Delta RH/\Delta T$ coefficient, the CTE can be reduced as well.

It is thus of great practical importance to control and possibly reduce the CTE at early ages. In this paper, a method for reducing the aforementioned increase of CTE is studied.

Internal curing by means of superabsorbent polymers (SAP), proposed by Jensen and Hansen [12,13], is an efficient method of introducing additional curing water into low w/c cement paste in order to compensate for part of the water consumed by cement hydration, e.g. [13–16]. As an effect, hydration of the material is promoted and self-desiccation and resulting self-desiccation shrinkage [17] can be controlled or even completely suppressed, which allows lowering the risk of early-age autogenous shrinkage cracking. The efficiency of the method is due to combining the thermodynamic and kinetic availability of water entrained within the SAP [15]. The latter aspect has been recently investigated and confirmed both experimentally [18–21] and using poromechanical modeling [22]. Additionally to the original application for controlling autogenous shrinkage, SAP have been proposed [12,23–25] as a method for air-entrainment and enhancing freeze–thaw resistance, since some types of SAP form empty voids of the desired size after the water is released.

This paper shows that the limiting effect of SAP on self-desiccation can be of great use not only for reducing autogenous shrinkage but also for reducing the thermal expansion of the material. In a previous study by Cusson and Hoogeveen [5], internal curing by means of light weight aggregates (LWA) had apparently no influence on the CTE of concrete, hence it was consequently neglected in a further study of the deformations of concrete with LWA [26]. With SAP, a very pronounced positive effect is obtained and presented here.

The concept applied in this work is very simple and is schematically displayed in Fig. 2. Since the $\Delta RH/\Delta T$ coefficient and hence also the CTE are increasing considerably with decreasing RH in pores, by eliminating or at least reducing the RH decrease, it is possible to control the $\Delta RH/\Delta T$ coefficient on levels close to zero and accordingly maintain almost constant, low values of the CTE during the first days of hydration. In other words, the overall CTE is reduced by reducing its moisture-dependent component, namely the $\Delta RH/\Delta T$-related component, which is done by maintaining high RH levels in the pores [3]. The proof of concept displayed schematically in Fig. 2 is provided by comparing directly the CTE of cement pastes and mortars with and without SAP addition, at different w/c.

To the authors' best knowledge, this is the first application where SAP are used for limiting the evolution of the CTE. The applicability of the method in practice can be of great advantage since it allows reducing considerably the thermal deformations and the risk of thermal cracking.

In this paper, the influence of SAP on hydration evolution, elastic modulus, self-desiccation and autogenous deformations measured using linear method [27,28] in cement pastes and mortars is presented and discussed in order to refer briefly to the current state of practice regarding SAP application and performance. Next, the innovative aspect of SAP application is investigated and discussed.

The CTE in cement pastes and mortars is measured using both volumetric [9] and linear methods. It is shown that, when SAP are added, the internal RH is kept at the levels close to 100%, and hence according to the scheme in Fig. 2, the moisture-related CTE is eliminated and the overall CTE can be maintained at an almost constant level during the first days of maturing. On the contrary, the CTE after 1 day is increasing by more than 70% in the cement pastes and by about 50% in mortars without SAP.

Finally, the composite models proposed by Hobbs [29], and Rosen and Hashin [30] are applied for prediction of thermal deformations of the mortar, based on the measurements performed on cement pastes. This method yields a very good agreement of the predictions and experimental results and hence is shown to be a useful tool in practical applications. Based on the observed agreement for mortar, the results are also extrapolated for a case of an exemplary concrete.

2. Materials and methods

2.1. Materials and mixture composition

Cement paste and mortars were prepared using cement CEM I 42.5N with a modified Bogue-calculated composition [31] (by wt.%): C_3S: 60.8, C_2S: 12.5, C_3A: 4.76, C_4AF: 9.8, free CaO: 0.5, Na_2O eq.: 0.81 and Blaine fineness of 277 m^2/kg.

The workability of the w/c 0.25 and w/c 0.30 mixtures (with and without SAP) was controlled by replacing part of the mixing water with a liquid polycarboxylate-based superplasticizer (29% of dry mass).

Deionized water was used which for the case of volumetric measurements of CTE was additionally deaired by boiling and cooled down to room temperature [9].

Solution-polymerized SAP with irregular particle shapes of size 63–125 μm were used. Absorption in cement pastes was determined as 16 g/g based on an unpublished study performed with synchrotron X-ray tomography. In this study the volume of a small (5 mm in diameter) cylinder filled with w/c 0.28 cement paste made of the same materials as used here with added SAP was investigated with X-ray tomography short after mixing. The volume of the swollen SAP particles was then determined and their total pore solution absorption was calculated based on the volumetric ratio occupied by the SAP in the cylindrical sample.

In mixtures with SAP the entrained water was added in an amount of $(w/c)_e$ 0.05, in addition to the basic w/c ratios of 0.25 and 0.30.

The aggregate used in mortars was alluvial sand from Switzerland composed of dense sandstone 37%, limestone 37%, dolomite 18% and metamorphic rocks 8%, with well-rounded particles of size 0.25–1.0 mm. Due to removing the finest fraction of aggregates, the water absorption determined according to EN 1097-6 was only 0.6% and the dry density was 2659 kg/m^3.

Except for the aggregates added, the mortars had the same composition as the corresponding neat cement pastes, including amounts of superplasticizer.

Mixing was performed using a vacuum mixer (Twister Evolution) with a 0.5 l vessel. All dry constituents were mixed manually for about 1 min before water was added, followed by 2 min of wet mixing under vacuum at 450 rpm.

Mixing and all experiments were performed in controlled-climate rooms at 20 ± 0.5 °C and 70 ± 5%RH.

The characteristics of the tested mixtures are presented in Table 1.

2.2. Setting time

Setting time of the cement pastes was determined by Vicat needle, similarly as described in EN 196-3. A slight modification of the method consisted of covering the surface of the sample with a plastic food wrap in order to limit water evaporation throughout the measurement. The thin foil did not hinder the penetration of the needle. The measurements were taken automatically at time intervals of 5 min. Two specimens were examined for each case.

2.3. Linear autogenous shrinkage

Linear autogenous shrinkage of mortars was measured using the corrugated tube method [27,28]. The deformation was measured on a stainless steel bench, which can accommodate three specimens in parallel, with two linear variable differential transformers (LVDTs) and a digital transducer indicator for each specimen. The setup was similar to that proposed in [28]. The measuring bench was placed in a silicone oil bath, which allowed reducing moisture loss from the tubes and at the same time maintaining stable temperature during the measurement. Automatic measurements allowed recording the deformation at the interval of 1 min starting from about 30 min from mixing. Nevertheless all the results regarding shrinkage are referenced to the length at final set in order to comply with the well-established standard ASTM protocol [27]. Two specimens were measured for each mixture. Independent mixing was performed for each specimen.

Table 1
Characteristics of the tested mixtures.

Characteristic/Mixture	w/c 0.25	w/c 0.25SAP	w/c 0.30	w/c 0.30SAP	w/c 0.35	w/c 0.45
Superplasticizer (wt.% of cement)	1.9	1.9	0.5	0.5	0	0
Basic w/c	0.25	0.25	0.30	0.30	0.35	0.45
Entrained w/c	–	0.05	–	0.05	–	–
Total w/c	0.25	0.30	0.30	0.35	0.35	0.45
Aggregate fraction in mortar (vol.%)	–	–	40	38	38	35

2.4. Internal RH evolution

Measurements of internal RH in cement pastes and mortars were performed using water activity AW-DIO and HC2-AW sensors (for cement paste and mortars, respectively) by Rotronic. Each examined material was measured at two stations in parallel. The nominal accuracy of the sensors was ±1%RH and 0.8%RH for AW-DIO and HC2-AW sensors, respectively, and ±0.1 °C for both types of sensors. It needs to be however noted, that with these sensors higher accuracy is expected as RH decreases. The sensors were calibrated at the beginning and at the end of each measurement with three saturated salt solutions with equilibrium RH in the range 98–85%. This procedure allowed reducing the difference between two sensors measuring the same material to levels not exceeding 0.5%RH at most and usually much lower. The temperature of the sample and the sensor was maintained on the level of 20 ± 0.05 °C by means of a thermostat-controlled water bath with water circulating in the casings of the measuring chambers.

Right after mixing, the material was cast in sealed plastic containers. At the age of approximately 20 h the material was crushed into pieces of about 2–5 mm and about 8 g of crushed material was used for each examined sample. The specimens were next closed in sealed measuring chambers and the measurement continued until the age of 7 days or more. The readings were logged every minute with a HygroLog logger by Rotronic.

The mass loss in the specimens after the measurement was similar for all samples and did not exceed 0.07% of the initial mass of the sample in any case. Based on unpublished sorption isotherms data, such loss of water mass may correspond to a decrease of internal RH of less than 0.8%RH.

2.5. Volumetric CTE

The technique for measuring CTE used in this study was developed by Loser et al. [9] and is in general based on a recently-developed method for assessing autogenous deformation in cement-based materials [32]. It consists of casting small amounts (20–30 g) of cement pastes or mortars into elastic membranes. The specimens are next immersed in a silicone oil bath and suspended from a high-precision balance. By changing the temperature of the oil bath, the sample can be subjected to repeated temperature cycles of programmed amplitude. Based on the measured changes of the temperature and the apparent weight of the sample and using Archimedes' principle, the CTE can be calculated with good accuracy. The technique has been described in detail in [9], hence only its main features are summarized here.

The samples for the volumetric CTE measurements were cast into commercially-available condoms made of polyisoprene (Durex Avanti Ultima). The lubricant covering the condom was removed using a paper towel. During pouring of the fresh material into the condom, attention was paid to avoid entrapment of air bubbles. Next, the condom was closed using a metal clamp and a nylon string was attached to suspend the specimen from the balance. The weight of the immersed specimen and temperature of the oil beside the specimen were recorded every minute starting from about 15 min after water addition until an age of about 7 days. The temperature of the bath was changed between 17 and 23 °C in cycles lasting 60 min.

After the measurement, processing of raw experimental data consisted generally of the following steps, similarly as in [9]. First, the volume of the sample at each time step was calculated using the measured weights and temperatures and accounting for the volume of the membrane, closing clamp and string. The linear CTE was determined assuming isotropic behavior of the material, i.e., as one third of the volumetric CTE. Next, the experimental data regarding calculated volumes were limited to the points from the last 30 min of each 60 min temperature cycle, to consider only the measured points after the equilibration of sample temperature could have taken place. These chosen experimental points were then divided into two separate envelopes, corresponding to maximum contraction and maximum expansion volumes at the lower and upper temperatures, respectively. As an effect, each experimental envelope was composed of groups of 30 experimental points each, with the interval between groups equal to 90 min.

It is worth noticing that, even after equilibration of the temperature in the sample, equilibration of deformation could not be observed in principle. This is due to the fact that the thermal deformations caused by the cyclic temperature change, even if assumed not to be influenced by any delayed thermal effect in the time scale of 1 h, are superimposed to the continuous autogenous deformations. In order to account for this fact and obtain a continuous evolution of the CTE in time, periodic gaps between the groups of experimental points at each of the two envelopes needed to be interpolated. This was performed using cubic smoothing splines, independently for each of the two envelopes. As an effect, two approximated continuous envelopes were obtained, and the distance between them defined the volumetric deformation of the sample due to the change of temperature. It also allowed eliminating the noise due to the scatter of experimental data. The fitting procedure was written in the Python programming language and the smooth spline approximations were obtained using the *splrep* function of the *scipy.interpolate* package [33]. While fitting the approximated envelopes to the experimental data, a tradeoff between the closeness and the smoothness (smoothing condition) was satisfied by setting the residual sum of squares to be less or equal 4×10^{-3}% of the overall mean value from the experimental data.

2.6. Linear CTE

Prisms of size 15 × 15 × 160 mm^3 were cast in steel molds on a vibrating table. Three specimens for each material were prepared. After casting, the molds were kept at RH > 95% and 20 ± 0.5 °C. At the age of approximately 1 day the specimens were demolded and closed in hermetic plastic bags. At the age of 2 days, in order to prevent moisture loss or absorption of oil during the tests, the specimens were wrapped with aluminum tape (with an underlying layer of glue preventing the aluminum from getting into contact with the cement paste). Next, stainless steel gauges were glued at the ends of the samples and then the specimens were put in a silicone oil bath where the temperature was cycled between 15 and 25 ± 0.1 °C. Each temperature step lasted 1 h; after that time the specimens were taken out of the bath and their length was rapidly measured with a manual dilatometer. A single measurement lasted about 15 s. Additionally, the use of silicone oil in the bath allowed avoiding evaporative cooling of the sample. Several cycles per day were performed in this way. At this point, the CTE was calculated from the length change between the temperature steps, divided by the temperature difference, 10 °C, and by the sample length. In between the cycles, the specimens were left in the oil bath at 20 ± 0.1 °C.

2.7. Elastic modulus

The elastic modulus in compression was measured on sealed prisms of size 25 × 25 × 100 mm^3 at 1, 3, 7 and 28 days from mixing. Two samples for each material were tested.

2.8. Hydration evolution

The rate of heat release was measured on cement pastes with isothermal calorimetry at 20 °C using a TAM Air Isothermal Calorimeter by Thermometric AB. About 6 g of freshly-mixed material was put into glass vials of internal diameter 22.5 mm, closed and placed in the measuring cell. Two specimens for each material were tested, yielding a difference for the ultimate value of the cumulative heat of hydration of less than 2% at most.

3. Experimental results and discussion

3.1. Evolution of hydration degree and elastic modulus

As can be seen in Fig. 3, the application of internal curing has an almost negligible effect on the initial stages of cement hydration, with only a slight retardation of maximum heat flow visible for the w/c 0.25SAP cement paste. A promotion of hydration can be observed starting from the deceleration period, i.e., at the age of approximately 1–1.5 days. The offset peak for w/c 0.25 and w/c 0.25SAP cement pastes is the effect of the increased superplasticizer amount which delayed the hydration rates. It can be also observed, that the total heat released by the cement in w/c 0.25SAP and w/c 0.30 cement pastes, i.e., the pastes with the same total w/c ratio (see Table 1) is very similar. Hence, in terms of promoting hydration, internal curing has a similar effect to a simple increase of w/c ratio. This effect can be also predicted using Powers' model, see [12,17]. Assuming similarly as in [12] that the effect of internal curing with SAP on the ultimate degree of hydration in a sealed material (so-called closed system) is equivalent to the free access to water (so-called open system) in a mixture with the same basic w/c but without SAP, the ultimate degrees of hydration achieved in the tested samples can be predicted, see Table 2. It can be than seen that the expected ultimate degree of hydration is the same for w/c 0.25SAP and w/c 0.30. These predictions agree well with the measured degrees of hydration at 7 days, having in mind that the latter ones are naturally not yet the ultimate values. The values of the degrees of hydration were determined by normalizing the heat released at 7 days, Fig. 3b, with the theoretical heat at full hydration, estimated as 454 J/g [34].

The influence of SAP on the evolution of the elastic modulus is presented in Fig. 4. The increase of porosity due to the application of SAP leads to a visible reduction of the mechanical properties. However, it can be deduced that the effect of w/c increase due to internal curing is similar to a conventional increase of w/c. This is shown by the very similar trends observed starting from the age of 3 days for w/c 0.30 cement paste and w/c 0.25SAP cement paste, where the same total w/c were used (see Table 1).

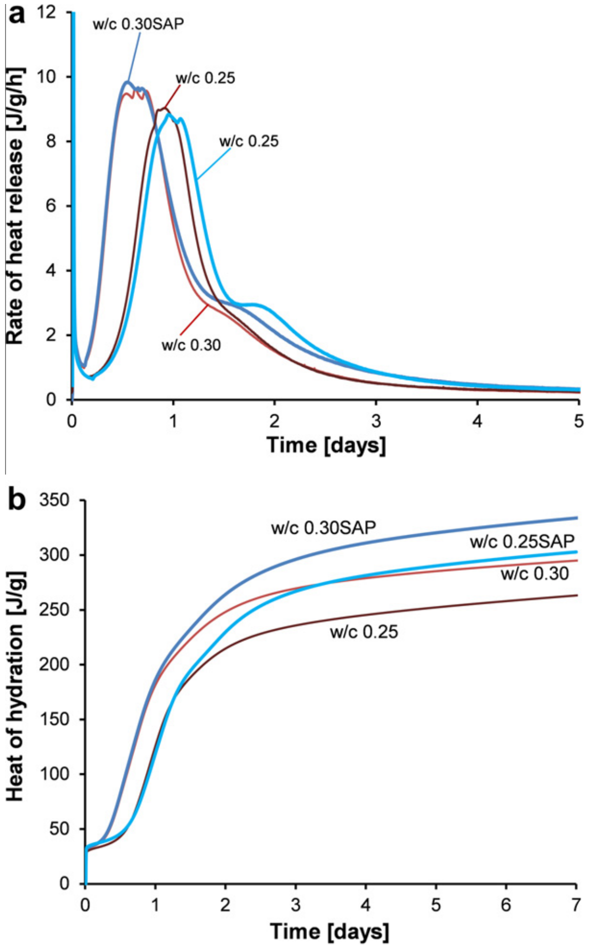

Fig. 3. Evolution of rate of heat release (a), and cumulative heat (b) in cement pastes. Average of two samples. Temperature 20 °C. Time from mixing.

3.2. Self-desiccation and self-desiccation shrinkage

In Fig. 5 the results concerning autogenous deformation are presented for w/c 0.30 and w/c 0.30SAP mortars. The deformations are referenced to the length at final set. Final set was determined with a Vicat needle on corresponding neat cement pastes as 8 h 10 min ± 5 min and 9 h 20 min ± 10 min for w/c 0.30 and w/c 0.30SAP, respectively. The setting times of the mortars were assumed equal to those for the corresponding cement pastes.

Possible origins of expansion occurring short after setting for both tested mortars, especially with SAP addition, may be reabsorption of bleeding water [35], some of which could be actually observed on the surfaces of the specimens, or crystallization pressure of calcium hydroxide [36]. The presented results show visibly higher swelling for the specimens with SAP than for the plain cement paste or mortar. Assuming both proposed mechanisms [35,36], this can be simply explained with the higher saturation levels (close to full saturation) maintained in materials with SAP, which hinders capillary pressure-driven shrinkage and hence makes the competitive swelling mechanism more apparent.

After approximately 1 day of maturing, self-desiccation shrinkage started surpassing the competitive swelling. In this period the effect of SAP addition on limiting self-desiccation shrinkage, especially important in terms of avoiding microcracking, is clearly visible, as is also illustrated by the internal RH measurements presented in Fig. 6.

While self-desiccation can be clearly observed for plain cement pastes and mortar, with its magnitude increasing with decreasing

Table 2
Predicted (Powers' model) and measured values of degree of hydration of cement pastes with and without SAP.

Mixture	Powers' ultimate degree of hydration	Measured degree of hydration at 7 days
w/c 0.25	0.60	0.58
w/c 0.25SAP	0.72	0.67
w/c 0.30	0.72	0.67
w/c 0.30SAP	0.86	0.73

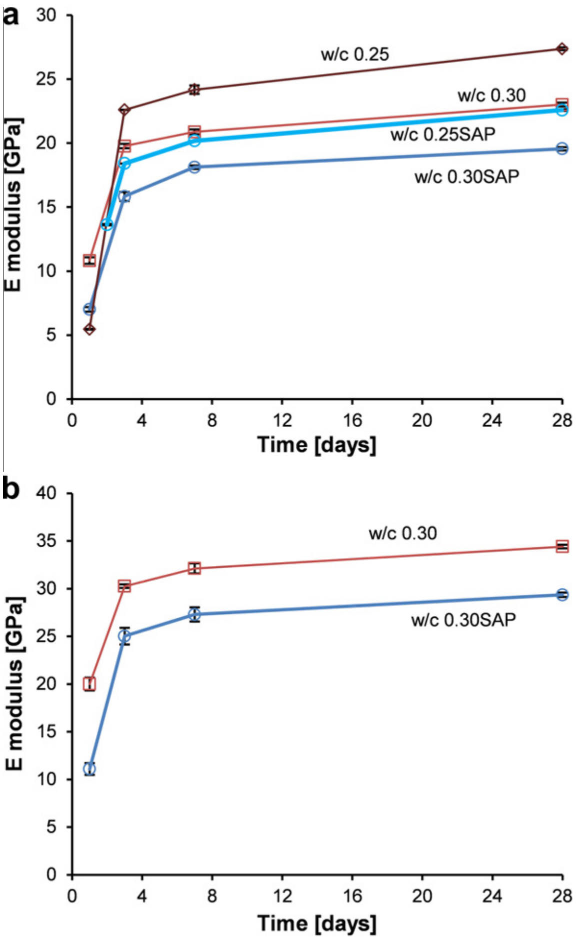

Fig. 4. Evolution of elastic modulus in cement pastes (a), and mortars (b). Average of two samples (standard deviation indicated). Time from mixing.

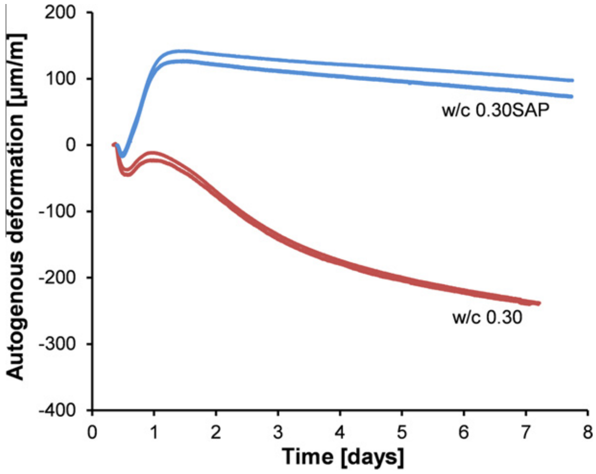

Fig. 5. Autogenous deformation in mortars after final set (duplicate specimens). Time from mixing.

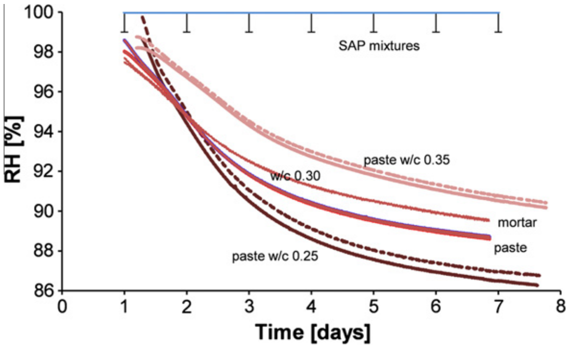

Fig. 6. Internal RH evolution in cement pastes and mortars (duplicate specimens). For all specimens with SAP (i.e., cement pastes w/c 0.25SAP, 0.30SAP and mortar w/c 0.30SAP) the reading was 100% RH over the whole period of measurement (presented together with the error bars showing nominal accuracy of the sensors).

w/c, for all the materials with SAP addition readings of 100%RH were taken along the whole period of measurements. It needs to be accounted for that the accuracy of the sensors at RH close to 100%RH is not possible to be determined, especially that the sensors were calibrated with saturated salt solutions at RH only up to 97.6%RH (obtained with a K_2SO_4 saturated solution). Moreover, the reading at such high RH levels in samples with SAP may have been influenced by vapor condensation on the sensor. Nevertheless, the results clearly show that the self-desiccation in materials with SAP addition can be effectively mitigated. As shown by poromechanical modeling performed in a recent study [16], the limiting effect of internal curing with SAP on autogenous shrinkage can be described exclusively with the latter hygral mechanism.

3.3. CTE

In this section, results regarding evolution of the CTE in cement pastes and mortars are presented, especially as affected by the SAP. As already shown by Loser et al. [9], the volumetric method, although prone to some aforementioned artifacts, is able to provide CTE results which are very close to those determined with a well-established linear method. Such comparison between methods based on completely different measurement principles was also performed in this study, Fig. 7.

It was observed that the CTE values determined with the linear method are consequently lower than those determined with the volumetric method. There may be several causes of this disagreement, which may originate from both methods. One of the factors that are essential in view of the volumetric technique reliability, as mentioned already in [9], is the proper determination of the density–temperature relation for the buoyancy liquid. The drift of the real buoyancy respect to that determined using reference materials may have a paramount influence on the magnitude of measured CTE, but much smaller on the observed trend. Further, the linear measurement requires that the samples are taken from the bath and measured manually, during which time they may cool down or heat up to equilibrate with the ambient temperature. Although the measurement was done within about 15 s, this should be taken into account as a possible cause for the lower values of the CTE. Finally, there is also a difference in initial conditioning of the specimens; the specimens for volumetric measurements are placed in a membrane and exposed to temperature cycles already some minutes after mixing, while the linear specimens are staying in molds in high RH regime for the first day after mixing,

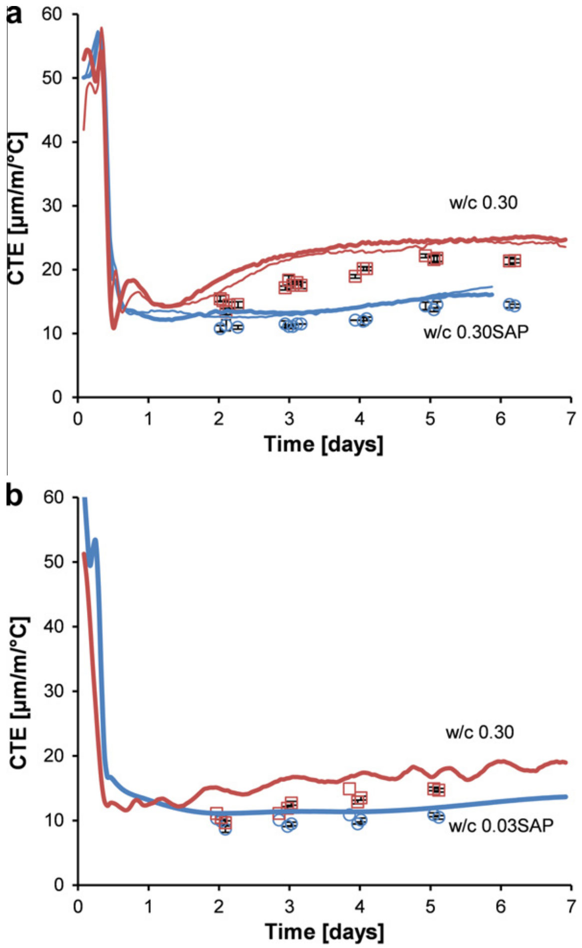

Fig. 7. Comparison of the linear method (points, average of three specimens) and the volumetric method (continuous lines) for (a) cement pastes (duplicate specimens), and (b) mortars (single specimens).

and are exposed to temperature cycles starting from the age of 2 days. Nevertheless it needs to be underlined that the trends of growing CTE with age are captured by the two methods in a very similar way. Application of both methods was necessary not only in terms of their validation, but also in terms of obtaining the results for a wide range of tested w/c ratios. The volumetric method allowed obtaining continuous evolution of the CTE in an automatized way. However, its application was limited to mixtures of lower w/c only. For w/c higher than 0.30, accumulation of bleed water between the sample and the membrane made the method inapplicable [9]. In such case, the linear method was the only possible way to examine the CTE evolution in mixtures of higher w/c.

As can be seen in Figs. 8 and 9, the CTE starts to grow in specimens without SAP both for the cement pastes and the mortars from the age of approximately 1–1.5 days. This is in agreement with e.g. [3,4] where it was observed that the CTE increases with the progress of desaturation of pores. The reason of this evolution is the so-called ΔRH/ΔT mechanism that was already briefly described in the Introduction, see also Fig. 2.

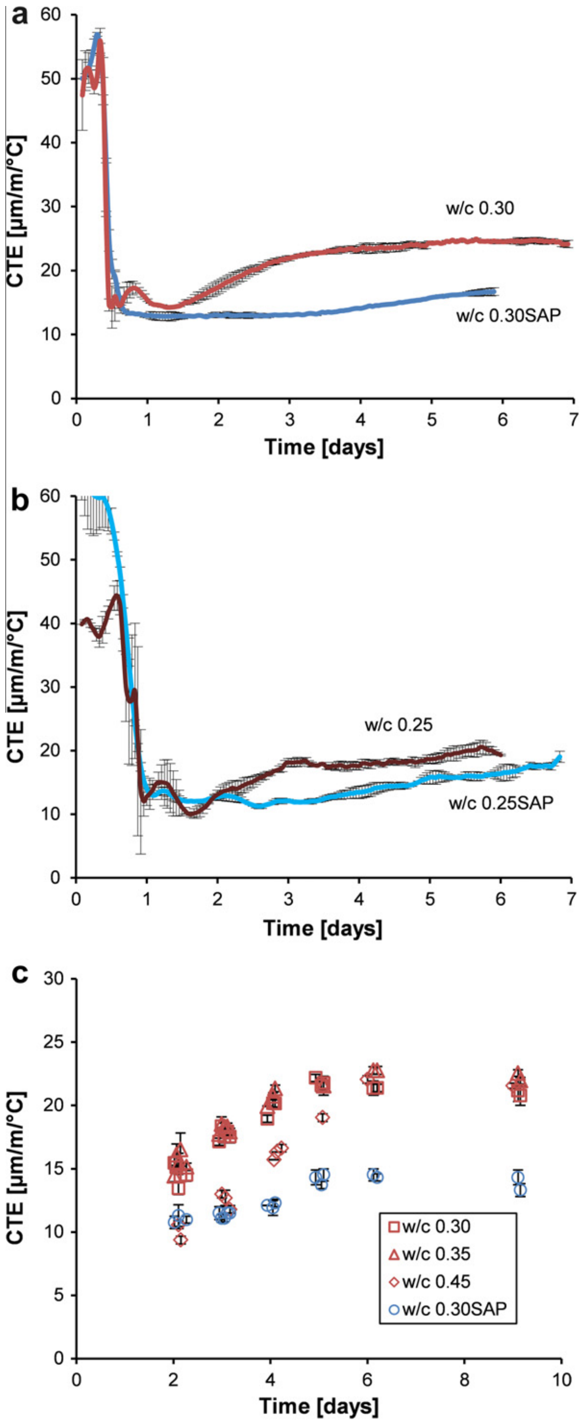

Fig. 8. Comparison of CTE of different cement pastes for volumetric (a and b) and linear (c) methods. In the volumetric method 2 samples and in the linear method 3 samples were tested for each material (average presented with standard deviation). Note that addition of SAP allows limiting the increase of the CTE after 1 day.

It can be observed that the CTE of the w/c 0.30 cement paste increases by about 60% between 1 day and 3 days and finally by more than 70% up to the age of 7 days. A similar trend, with the steepest increase from 1 to 3 days could be observed for the w/c 0.25 cement paste. In view of the governing ΔRH/ΔT mechanism, the steep CTE evolution in the period 1–3 days can be attributed to the corresponding steep decrease of the internal RH, Fig. 6. Even though the final values of the CTE for w/c 0.25 are lower, which is due to the higher stiffness, Fig. 4, the relative increment is similar to that of the w/c 0.30 paste. The high scatter observed at the initial stages of maturing for the w/c 0.25 cement paste is most probably the effect of bleeding occurring due to the high amounts of plasticizer used.

For the w/c 0.30 mortar, the CTE increases by about 50% from 1 day to 7 days, Fig. 9. The lower values of the CTE observed for the mortars than for the pastes are due to the lower, constant CTE of aggregates, which consequently restrain the deformation

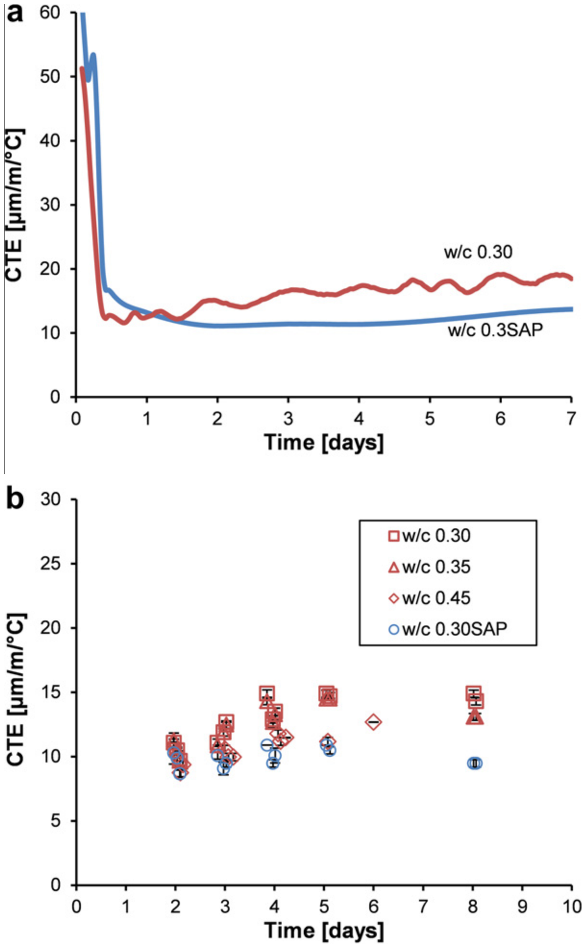

Fig. 9. Comparison of CTE of different mortars for volumetric (a), and linear (b) methods. In the volumetric method 1 sample and in the linear method 3 samples were tested for each material (average presented with standard deviation). Note that addition of SAP allows limiting the increase of the CTE after 1 day.

of the paste. This issue is studied by means of a composite models approach in the following Section 4. It needs to be realized, that due to the incompatibility of thermal deformations between the cement paste and the aggregates in concrete and mortar, even if the CTE of the composite is lower, there exists a risk of microcracking at the aggregate–paste interfaces, which can jeopardize the durability of the material, see also [37,38].

The results for w/c 0.30 mortar were in general more affected by experimental scatter than for the neat cement pastes, which is primarily due to the problems with filling the membranes with a stiff mixture (the investigated mortars had much stiffer consistency in comparison to the neat cement pastes). As a result, some air may have been entrapped between the membrane and the material which can result in measurement instabilities as those observed in Fig. 9, since the entrapped air or bleeding water are expanding or contracting with changing temperature. Another source of the instability of the determined CTE may have been due to the vibrations of the oil in the bath. These aspects have been dealt with in detail in [9].

The tests performed on higher w/c mixtures using the linear method, Figs. 8c and 9b, show that the increase of w/c to 0.35 has hardly any influence on limiting the evolution of the CTE. For w/c 0.45 some delay of the increase can be observed, which may be due to high RH during the first days, caused by the slower self-desiccation process and reabsorption of bleeding water. However the final values of the CTE are close for all mixtures without SAP.

The most interesting result revealed by the Figs. 8 and 9 is the effect of the SAP on the CTE, which can be regarded as a proof of concept of the presented paper. It is shown that internal curing with SAP allows practically eliminating the CTE increase within the first days of maturing, i.e., the period which is most essential from the point of view of thermal cracking risk. The effect of SAP on limiting the CTE both in cement pastes and mortars is illustrated equally clearly both with volumetric and linear methods.

Even if a small increase of the CTE occurs after about 4 days of maturing, which is most probably due to the fact that all entrained water is already consumed, see [16], the CTE is still maintained at a very moderate level. The origin of this fact is that the RH in pores is kept at very high levels, close to 100%, see Fig. 6, and hence the values of the $\Delta RH/\Delta T$ coefficient remain very low, which is schematically displayed in Fig. 2. At full saturation the RH is 100% and the $\Delta RH/\Delta T$ is zero, while it increases with decreasing saturation and RH in materials without SAP [3,4,9]. This issue is also investigated in a parallel study [39], where the changes of RH due to temperature are examined in detail. The elimination of the $\Delta RH/\Delta T$-related CTE, obtained exclusively with SAP, is so efficient that it allows reducing the CTE even though the stiffness of the material with SAP is reduced in respect to the reference, plain cement paste or mortar, Fig. 4.

4. Modeling

It is generally known that, as presented in the previous sections, mortars (and hence also concrete) are characterized by higher elastic modulus E and experience lower shrinkage and thermal deformations than plain cement pastes at comparable w/c. It is shown in this section, that the thermal deformation of the composite, i.e., mortar, can be predicted based on the behavior of the cement paste and properties of the aggregates, using composite models [29,30]. In calculations of the CTE of the mortars, the CTE and the elastic moduli for cement paste are the model inputs that are based on the actual determined experimental data, with the evolution of the latter parameter approximated with fitted curves, Fig. 10. In lack of the appropriate data, the following four parameters need to be assumed according to literature: Poisson ratio of cement paste and Poisson ratio, E modulus and CTE of aggregates.

The assumed values of the first three parameters to be further used for modeling the CTE can be first validated by modeling the elastic modulus evolution in the mortars. Hobbs [29] proposed the following relation for predicting the elastic modulus of a composite:

$$E_c = E_m\left[1 + \frac{2\phi_a(E_a - E_m)}{E_a + E_m - \phi_a(E_a - E_m)}\right] \tag{1}$$

where subscripts m, a and c denote cement paste matrix, aggregates and composite, respectively and ϕ is the volume fraction of the constituent.

Hashin and Shtrikman [40] developed the equations defining the bounds for bulk modulus K and shear modulus G. After some simple transformations, the relations for the bounds of elastic modulus can be obtained:

$$E_c \geqslant 3(1 - 2\nu_c)\left[K_m + \frac{\phi_a}{(K_a - K_m)^{-1} + 3\phi_m(3K_m + 4G_m)^{-1}}\right] \tag{2a}$$

$$E_c \leqslant 3(1 - 2\nu_c)\left[K_a + \frac{\phi_m}{(K_m - K_a)^{-1} + 3\phi_a(3K_a + 4G_a)^{-1}}\right] \tag{2b}$$

with Poisson ratio of the composite ν_c assumed equal to that of a plain cement paste. The modeling is applied for the case of w/c 0.30 and w/c 0.30SAP mixtures. The mechanical properties of the

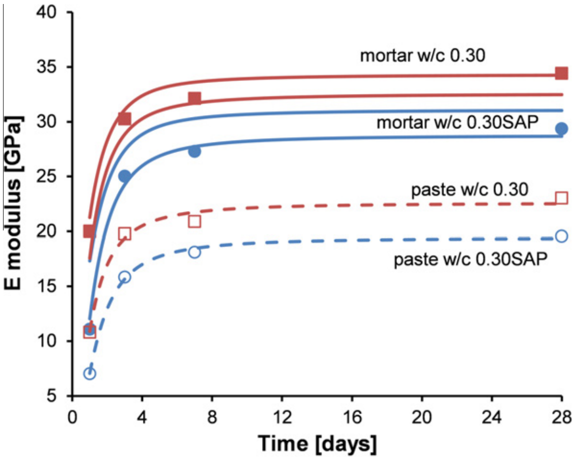

Fig. 10. Predictions of the elastic moduli of mortars using Hashin–Shtrikman lower and upper bounds [40] (continuous lines) compared to the experimental data from Fig. 4 (points). Input data on cement pastes was approximated with fitted curves (dashed lines). Note that the Hobbs' model [29] (not presented here) overlaps with the lower bounds of the Hashin–Shtrikman model.

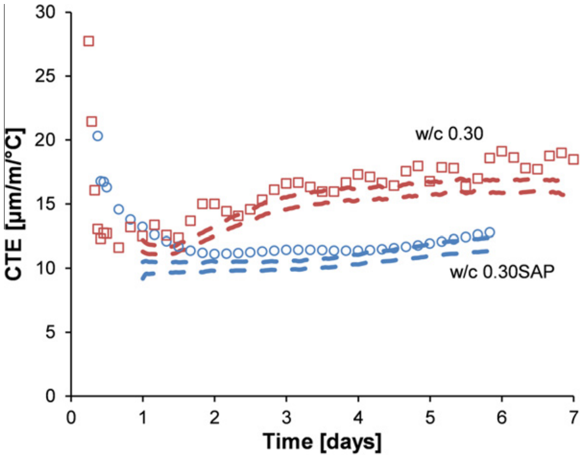

Fig. 11. Predictions of the CTE of mortars using the Rosen–Hashin model [30] (lower and upper bounds, dashed lines) compared to the experimental data from Fig. 9a (with reduced number of experimental points for better clarity). Note that the Rosen–Hashin upper bound overlaps with Hobbs' [29] predictions (not presented here).

cement pastes were calculated based on the measured evolutions of elastic moduli, Fig. 4, approximated with fitted curves, Fig. 10, and published data on the evolution of Poisson ratio v [41]. The latter parameter was measured in [41] using an ultrasonic-based technique on w/c 0.35 white cement pastes. Based on the composition of the aggregates, their mechanical properties were assumed as E_a = 60 GPa [42] and v_a = 0.2 [29]. In Fig. 10 the results of the modeling are presented. Hobbs [29] noted that for the case of $v_m = v_a = v_c = 0.2$ the predictions of his model are equal to the lower bound of the Hashin–Shtrikman model [40]. Indeed, even although the Poisson ratio assumed here for the paste was especially at early ages higher than for the aggregates (i.e., about 0.28 at 1 day and 0.20 at 28 days), it leads to a negligible difference between the two predictions. Hence, the Hobbs' model [29] predictions are not presented since they overlap with the lower bound of the Hashin–Shtrikman model [40]. It can be seen that the assumed parameters allow obtaining a reasonable agreement of the modeled and experimental data for the two mortars tested.

Having validated the assumed mechanical parameters of cement paste and aggregates, Fig. 10, modeling of the CTE can be performed. For this purpose two models are applied: the Hobbs' model [29] (Eq. (3)) and the Rosen–Hashin bounds [30] (Eqs. (4a) and (4b)).

$$\alpha_c = \varepsilon_m - \frac{(\alpha_m - \alpha_a) \cdot \phi_a \cdot 2 \cdot K_a}{K_m + K_a + \phi_a(K_a - K_m)} \tag{3}$$

$$\alpha_c \leqslant (\phi_m \alpha_m + \phi_a \alpha_a) + \frac{4\phi_m \phi_a G_a (K_m - K_a)(\alpha_m - \alpha_a)}{3K_m K_a + 4G_a(\phi_m K_m + \phi_a K_a)} \tag{4a}$$

$$\alpha_c \geqslant (\phi_m \alpha_m + \phi_a \alpha_a) + \frac{4\phi_m \phi_a G_m (K_m - K_a)(\alpha_m - \alpha_a)}{3K_m K_a + 4G_m(\phi_m K_m + \phi_a K_a)} \tag{4b}$$

where α is the CTE. Based on volume averaging of the values of the CTE given in [42] for the specific rocks composing the used aggregates blend, the CTE of the aggregates can be estimated as within a range 6–10 µm/m/°C. The value of 9 µm/m/°C was assumed in the analysis because aggregates of low porosity were used and hence values closer to the upper range of the CTE given in [42] can be expected.

It appears that the Rosen–Hashin upper bounds [30] practically overlap with Hobbs' model [29], Fig. 11, similarly as observed for modeling elastic modulus in mortar, Fig. 10, hence the latter result is not presented here.

It can be seen in Fig. 11 that the models slightly underestimate the CTE values. However, the agreement can be still found very satisfactory, both regarding the trends and the absolute values of the CTE.

It needs to be naturally realized that such models as those used in this work are based on a series of simplified assumptions. One of the main assumptions is that the composite, i.e., the mortar, is composed of two phases which are homogenous, namely aggregates dispersed in the cement paste matrix. The other simplifications and resulting limitations are due to the assumed isotropy and elastic behavior of the inclusions and the matrix. The models assume no influence of shrinkage and microcracking on the stiffness, perfect bond between the matrix and inclusions, and no percolation of the inclusions, to name only the most important limitations. However, since a very good agreement between the predictions and the experimental data was obtained in this study, it can be assumed that the aforementioned effects are of lesser importance for the examined set of materials.

Taking into account the very good agreement obtained for the CTE using the Hobbs' model [29], one could estimate the CTE of an exemplary w/c 0.30 concrete, similar as the tested mortars but with 67% of volume occupied by the aggregates as changing from about 10 µm/m/°C at 1 day to 13 µm/m/°C at 7 days. This approximately 30% increase could be naturally eliminated by using SAP.

5. Conclusions

The results presented in this study clearly show that the SAP can be effectively applied not only for limiting autogenous shrinkage, but also thermal deformations of cement pastes and mortars, and consequently also concrete. While the former application has been investigated in a series of studies, e.g. [13–15,25] following the work by Jensen and Hansen [12,13], to the authors' knowledge this works presents the first application of SAP to control the CTE of cementitious materials. This can be especially beneficial in low w/c mixtures, where due to self-desiccation and the RH dependence upon temperature, the CTE can increase substantially during the first days of maturing.

The results obtained both with the linear and volumetric methods show that in the plain materials without SAP the CTE increases after 1 day by more than 70% and reaches values of about

25 μm/m/°C at 7 days in a w/c 0.30 cement paste and increases by about 50% and reaches values of about 18 μm/m/°C at 7 days in a w/c 0.30 mortar. The steepest increase was observed in the period between the age of 1 and 3–4 days, where about 80% of the total CTE increase takes place, which agrees very well with the observed steepest decrease of internal RH due to self-desiccation. This increase is present in all investigated cement pastes and mortars without SAP, for w/c ratios from 0.25 to 0.45, with only some delay observed for the highest w/c of 0.45. It is then shown that the application of internal curing with SAP allows maintaining almost constant, low values of CTE during the first 3–4 days of maturing, followed by a moderate increase observed in some cement pastes. The reduction of the CTE increase is possible due to reducing the self-desiccation, and consequently controlling the increase of the $\Delta RH/\Delta T$ coefficient. It can be thus concluded that by reducing self-desiccation, the moisture-dependent part of the CTE is reduced. This observation can be of paramount importance in terms of applying SAP in practice. It appears that SAP can be applied not only when limiting the autogenous shrinkage is the goal, but whenever the thermal deformations need to be controlled as well.

The application of the two analytical composite models shows that the behavior of the mortar regarding thermal deformations can be predicted with a good accuracy based on the measured behavior of cement paste and knowing the volume fraction of the aggregates and their properties.

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