Influence of cement matrix composition on early age shrinkage properties

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Abstract. Early age shrinkage behaviour is an important factor in determining durability properties of cementitious composites. Shrinkage occurs in cement paste, but it can be tested in paste, mortar, and concrete. Differences in results obtained can be due to the mitigation influence of aggregates and other additions, like fibres. In order to better understand the early shrinkage properties on cementitious composites in use it is necessary to determine the influence of cement matrix composition. The use of mineral additives as a replacement for cement has been a practice for many years, which, in addition to improved mechanical properties of composites, also affects the reduction of waste and use of natural resources. Although similar to cement in composition, differences lead to variation in reactions during the hydration and thus to the shrinkage properties at early age. Delayed or accelerated reaction can be seen in temperature and humidity development and in values of shrinkage, autogenous as well as drying. Autogenous shrinkage was performed in accordance with modified HRN EN 12390-16 on prisms and ASTM C1698 on corrugated tube. Tests were performed on the cement paste of a reference mixture with w/b 0,3 and mixtures with different amounts of mineral additive as a cement replacement.

1 Introduction

Durable cementitious composites require changes in composition compared to conventional mixes. The use of mineral and chemical additives allows the reduction of the water- binder ratio, which makes it possible to obtain mixtures with high and ultra- high performance without negatively affecting the placing possibilities and properties in the fresh state. The use of additives alters the hydration process and, consequently, the volume deformations.

Volume deformations occur at the paste level, although they can also be measured in mortar and concrete. The lowest shrinkage values are observed in concrete mixtures due to a lower amount of cement paste and consequently lower chemical shrinkage, the presence of aggregates that have a limiting effect, and the effect of additives [1].

There are different types of volume deformations, depending on their origin and kinetics and also on the conditions under which they occur. These are chemical, autogenous, thermal, drying and carbonation [2]. Shrinkage can also be divided based on the time of occurrence into early and late. Early shrinkage is determined from the time of mixing to the first 24 hours, while late is everything after.

Immediately after cement and water are mixed, a series of complex chemical reactions occur that form hydration products and cause microstructure development. During the process, water is consumed and the volume of water decreases, while the volume of solid particles increases [3]. The absolute volume of hydration products is less than the total volume of cement and water before the reaction. This is due to the formation of hydration products with higher density and to the higher density of chemically bound water compared to free water [2], [4]. The difference obtained is called chemical shrinkage. In addition to the apparent volume decrease it is also visible in the formation of pores.

During the formation of the hydration products, bonds are formed between particles and the development of the solid structure begins. This time is defined with the setting time. Simultaneously, the development of mechanical properties such as strength and modulus also begin to develop. Although the properties are of low value, the cementitious composite will resist formed initial stresses or internal microcracks will occur.

After placement, gravitational forces and the local drying environment begin to affect the (micro) structure of a cement paste, mortar, or concrete [5]. The effects depend on the water- binder ratio, the concentration and particle size distribution of the solids and also evaporative water loss from the surface in relation to bleeding and drying conditions [5]. When drying is greater than the bleeding and curing water, this leads to a reduction of water in pores and the formation of menisci between the particles, creating capillary tension that compresses the surrounding solid [5], [6]. And when the sample is sealed, i.e., there is no exchange of matter with the surrounding environment, there is a decrease in internal relative humidity, a phenomenon called self- desiccation that causes capillary tension. The result of self- desiccation and formed stresses is autogenous shrinkage.

Autogenous shrinkage is defined as the deformation of the closed, isothermal cementitious material system that is not exposed to external influences and restraints [3],

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[4]. The deformation can occur as shrinkage or as swelling. Autogenous swelling is a short- term formation of hydration products when the bleed water is reabsorbed [3]. Significant settlement and bleeding are generally observed in cementitious composites without admixtures with a w/c > 0.4 [5]. Autogenous shrinkage is a concern in mixtures with lower w/c ratio. This is due to the denser matrix formed in mixtures with a lower water- binder ratio, increasing the hydrostatic tension forces (capillary tension) and leading to the self- desiccation [7].

The most commonly used approach to define autogenous shrinkage is capillary tension. It attempts to explicate the relationship between autogenous shrinkage and water movement. Capillary tension theory is based on the influence of pore structure, relative humidity, self-stress, degree of hydration and interface of components of a heterogeneous cementitious system [3]–[6]. In addition to the above mentioned, stiffness that enables the paste to withstand the stresses, also has a great influence on autogenous shrinkage. A major concern from autogenous shrinkage is the appearance of cracks at an early age that accelerate the ingression of water and harmful matter resulting in the deterioration of durability properties.

As previously mentioned, the addition of mineral and chemical additives has a significant influence on the hydration process, internal relative humidity and stiffness and consequently on autogenous shrinkage [7], [8].

Fly ash is a fine powder that is a by- product of coal combustion in thermal power plants. Its particles are regularly spherical or hollow and filled with smaller particles of various shades of grey. Fly ash affects the fresh and hardened state by actively participating in the hydration process. It is well known and often used as a cement replacement due to its pozzolanic reaction. A dosage greater than 50 % is considered a high- volume fly ash composite, but the optimum values are considered 15 to 30 %. The chemical composition should also be considered as it has a strong influence on the future composite properties [9]. It is generally agreed that the early age shrinkage is lower in composites containing fly ash due to lower cement content and water consumption and consequently slower hydration reaction, but after a certain time there is an increase in the reaction due to the pozzolanic properties which may manifest itself in increased shrinkage [8], [10], [11].

To better understand the influence of the cement matrix composition on early age shrinkage, measurements of autogenous shrinkage were performed on mixtures with fly ash as cement replacement, while the water-binder ratio was kept constant. Measurements of setting time, change in internal relative humidity, autogenous shrinkage in prisms and corrugated tubes were performed and are discussed in the paper. A comparison of two methods for measuring autogenous shrinkage was also made in relation to the different experimental setups and determination of time zero.

2 Materials and Methods

Laboratory tests were performed with three cement paste mixtures differing in binder. The following components were used: CEM I 52.5 N cement, superplasticizer based on modified polycarboxylic ether (PCE) polymers, tap water, and fly ash as a supplementary cementitious material. All three mixes were prepared according to the same composition with different binder ratios, Table 1.

Table 1. Cement paste composition.

Component	**Binder**	**Water**	**SP**
[kg/m^3]	550	165	2.31

The water-binder ratio of all mixes was 0.3 and the proportion of superplasticizer was 0.42 % by weight of the binder. All three mixes were prepared according to the standard procedure [12]. The designation of the mixes was based on the percentage of cement replacement by fly ash, as follows:

M1 – reference mixture, 100 % cement
M2 – a mixture with 15 % fly ash and 85 % cement
M3 – a mixture with 30 % fly ash and 70 % cement

For all mixes, the fresh density, temperature and setting time were measured. In addition, the paste was cast into prismatic moulds of 4x4x16 cm to measure compressive and flexural strength (HRN EN 1015-11 [13]). After casting, the specimens were covered with plastic foil under laboratory conditions (temperature 20±2 °C) for 24 hours until demoulding to prevent water evaporation. After demoulding, specimens for strength tests were stored in a humid chamber at 20 ± 2 °C and RH ≥ 95 % until 28 days of age.

The remaining tests, relative humidity change and autogenous shrinkage, were prepared and set for automatic measurement from the time of mixing until 5 days of age. Relative humidity was measured on two samples using the Rotronic measuring station HC2-AW-(USB). The paste is cast in a mould, which is placed in the chamber of the measuring device and closed with the measuring head, which has sensors and an additional mechanical seal. Similar test setups were also used in previous literature [6], [8], [14], [15]. The evolution of temperature was monitored on prisms and tube specimens since autogenous shrinkage is affected by the thermal expansion and contraction caused by the temperature change due to the hydration reaction.

Autogenous shrinkage was measured on prisms with dimensions 4x4x16 cm according to modified HRN EN 12390-16 [16] and on corrugated tubes 430 mm long and 29 mm in diameter according to ASTM C1698 [17]. Prism specimens were sealed with thin plastic foil and adhesive tape while corrugated tube specimens were sealed with end plugs and additionally with Parafilm®. All specimens were stored under the same conditions and the measurement was performed on three samples and the mean value is shown. It should be noted that there was a power cut during the autogenous shrinkage and internal RH test of mixture M2, resulting in the loss of some data. The missing data was successfully filled in based on the property trend line. The results of autogenous shrinkage are presented from the beginning of the measurement, from the final setting time and as a function of the change in relative humidity and temperature.

3 Experimental Results and Discussion

The properties of the cement pastes are presented in the following. Fresh density and temperature do not show much difference in all the mixes. The values for fresh density are 2.098, 2.044 and 1.979 g/cm^3 for the M1, M2 and M3 mixes, respectively. The lower values (2.58 % and 5.70 %) can be explained by the lower density of the fly ash and the delayed hydration reaction. This is also evident when setting time is observed (Figure 1). In relation to the reference mixture, the final setting time was longer +1:13:03 and +4:52:36 for M2 and M3, respectively. The delayed setting time was greatest for the mix with the highest percentage of fly ash (M3). Such behaviour has been observed in other studies in the literature [7], [8], [11].

The influence of fly ash is also visible in the strength values. Delayed formation of hydration products delays hardening so that the expected strength values after 28 days are lower than the reference values, while higher values can be expected at a later age [18], [19]. The reason for this behaviour is the influence of fly ash on the hydration process, due to the lower cement content and available $Ca(OH)_2$ needed for the continuation of the hydration process.

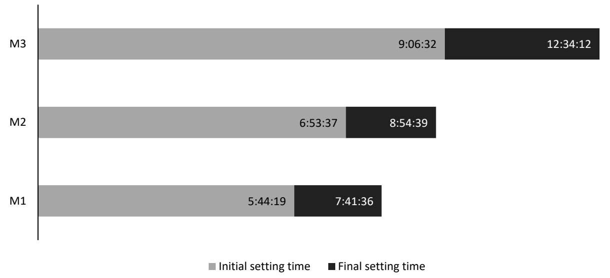


Fig. 1. Setting time of the mixes.

The temperature evolution was measured on the prisms and corrugated tube specimens over time and is shown in each of the following figures, 2a and b. The developed temperature and heat capacity depends on the binder, it can either increase or decrease, while the w/c ratio mainly affects the heat capacity of water and its influence decreases when the water is bound in hydration products [5]. From the graph shown in Figure 2b, it can be seen that the delayed hydration also results in a delayed occurrence of the temperature peak for the M2 and M3 mixtures. Finally, the mixture with 30 % fly ash content reaches the lowest temperature, which is also reflected in the measured shrinkage values.

The values of autogenous shrinkage were measured shortly after mixing up to 5 days, Figure 2. This time prior was necessary to prepare and perform the test. It can be seen from both figures that shrinkage increases rapidly in the first few hours and then decelerates over time. Comparing the reference and fly ash mixtures, a correlation between the results measured on prisms and corrugated tubes is evident. Figure 2 shows that the addition of fly ash has a positive effect on shrinkage. The higher the proportion of fly ash, the lower the shrinkage value.

For the results to be comparable with the existing literature, it is necessary to determine the time zero, corresponding to the start of autogenous shrinkage. It has long been clear that the measurement of autogenous shrinkage after demoulding, i.e., after 24 hours, is too late. However, when the cementitious composite behaves like a liquid, during the first hours, the changes are usually great in value but not significant [10], [20]. Due to the fluidity of the mixture at an early age, any change caused by generated stresses can be compensated.

As mentioned earlier, autogenous shrinkage is the shrinkage of a formed matrix skeleton caused by self-desiccation [2], [4], [8]. The development of the cement paste structure includes the setting of the cement paste system, the formation of a solid hydrated matrix, the development of porosity and the increase of strength. The formed pores are initially filled with water, but the continuation of the hydration process leads to a decrease in the internal relative humidity and a process of self-desiccation [2], [4], [5].

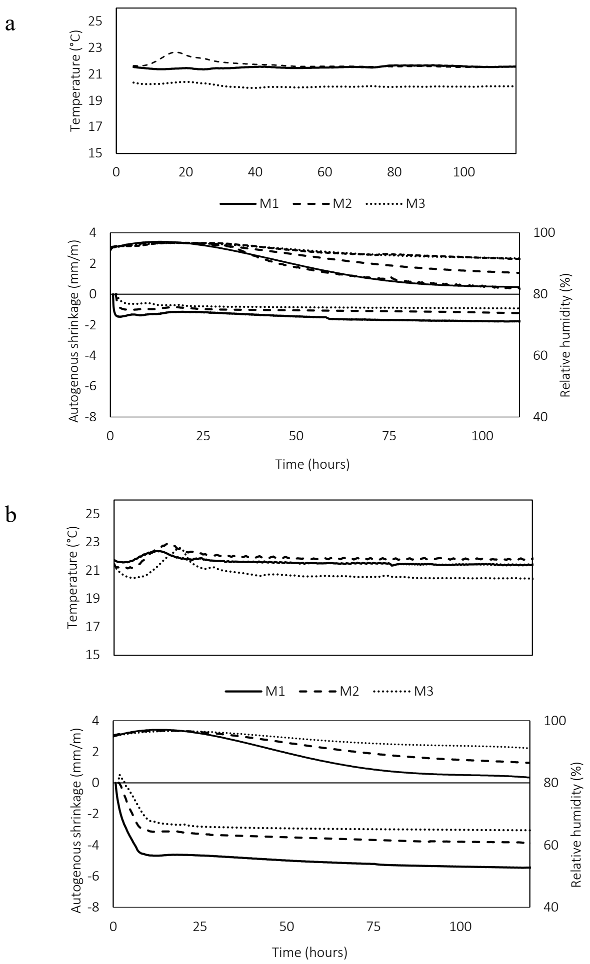
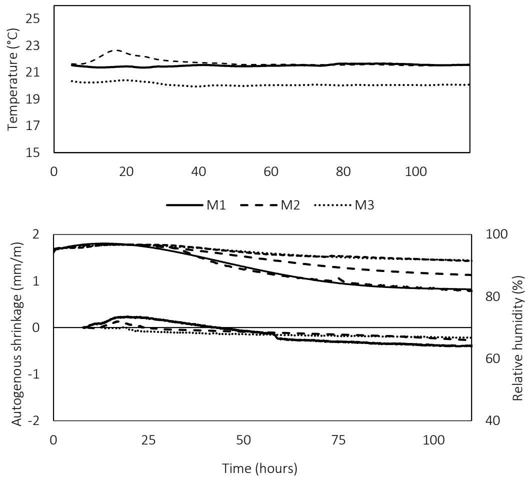


Fig. 2 Autogenous shrinkage, temperature, and relative humidity measured on a) prism and b) corrugated tube specimens.

The onset of autogenous shrinkage, i.e., time zero, is defined by the final setting time as given by the standard, which corresponds to skeleton formation and the decrease in internal relative humidity that accompanies self-desiccation [17]. There is a certain time span between the final setting time and the decrease in internal relative humidity during which different behaviour tendencies occur. Such behaviour was also observed in this study. The reason for such behaviour could be the shape and volume of the tested sample. The temperature evolution in the bulky sample used for determining the setting time with the Vicat needle leads to slightly accelerated hydration compared to paste in a tube and a prism which is why setting there appears later [21].

a



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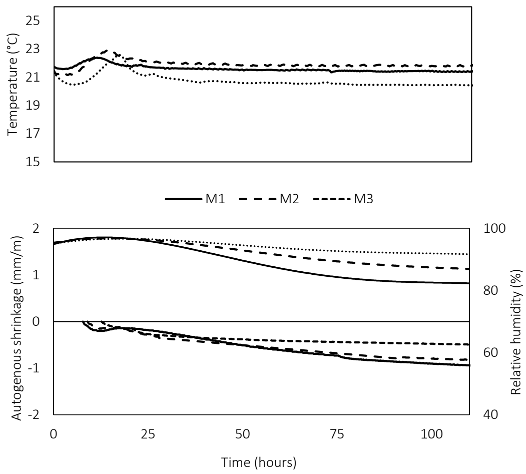

Fig. 3 Autogenous shrinkage measured from final setting time on a) prism and b) corrugated tube specimen.

Final setting time and relative humidity results were used to interpret both methods of measuring autogenous shrinkage. A higher drop in internal RH indicates smaller pore sizes being emptied and higher autogenous deformations as more self- desiccation occurs [18]. Such behaviour is associated with a slower reaction when fly ash is used as a cement replacement because it consumes less water and causes a different pore size distribution [18]. This is evident in the autogenous shrinkage results shown in Figure 3.

In the prism specimens (Figure 3), swelling of the M1 and M2 mixture is observed initially, which can be explained by reabsorption of the bleed water. After swelling, shrinkage occurs, about 20 hours after mixing. The M3 mixture shows a different trend. Here, the initial changes are characterized by a rapid onset of shrinkage and a low and short onset of swelling, which then continues to shrink. The highest final shrinkage values are seen in the reference mixture, followed by M2 and the lowest in the M3 mixture (Figure 3a).

From Figure 3b it can be seen that from testing autogenous shrinkage on corrugated tubes, the effect of bleeding can be reduced. The specimens were rotated 180° by hand before starting the measurement. The results obtained show similar behaviour compared to the results obtained on prisms. The greatest shrinkage after 5 days was observed in mixture M1. However, the results show that a 15 % cement replacement by fly ash is not sufficient to significantly improve the shrinkage properties at early ages.

According to the work of Huang et al. [15] and Lv et al. [10], the final setting time determined by the automatic Vicat apparatus is not the best indicator of the onset of shrinkage, because the rate of the shrinkage around the final setting time is generally high with large deviation. Also according to the work of Holt [1], if there was still bleed water at the time of setting, the reference point should not be determined until the bleed water is fully reabsorbed. Then time zero should rather be determined by the decrease in internal relative humidity.

Considering the decrease in internal RH, the analysis was performed using values obtained when a 0,5 % drop of the internal RH was determined. This corresponds to the point of 18.25, 18.30 and 20.0 hours after mixing for M1, M2 and M3 mixture. If the values of shrinkage on prisms were considered as shown on Figure 4, values would be 0.6769, 0.4288 and 0.1962 for M1, M2 and M3, respectively. Thus, the higher the fly ash replacement, the lower the shrinkage value. Shrinkage reduction in corelation to the reference mixture is 37 % and 71 % for M2 and M3.

The results of shrinkage obtained on the corrugated tube samples (Figure 4b) are in accordance with the results obtained on prisms, although slightly higher in value.

If autogenous shrinkage was observed along with a change in internal relative humidity, it can be seen that the reference mixture exhibits a greater decrease in internal relative humidity compared to mixtures containing fly ash (Figure 4). The final value of internal RH was 80 %, 85 % and 90 % for the mixtures M1, M2 and M3, respectively. The higher the percentage of fly ash, the higher the internal RH value and the lower the change is. The difference in internal relative humidity after 5 days was 16.95 %, 12.34 % and 7.12 % for the M1, M2 and M3 mixtures, respectively. The obtained results are in accordance with the previous study [10] and the assumption of lower water consumption.

Also, it can be seen that the onset of shrinkage is in good relationship with the decrease in internal RH, but also the overall shrinkage measured on prisms is consistent with the overall change in RH (Figure 4).

Comparing the results obtained measuring autogenous shrinkage on prisms and corrugated tubes, it is evident that values on prisms are lower than those on corrugated tubes. The difference in value of the two methods is most likely due to measurement settings, friction, bleed water and moisture loss prevention [20], [22]. Furthermore, it is known that the use of contact sensors may damage cement- based materials at an early stage and produce relative displacement when measuring heads are inserted [22]. It should also be considered, as shown in the work of Wyrzykowski [21], that autogenous shrinkage measured on cement paste with w/c = 0.3 on unrotated samples showed lower values compared to rotated ones.

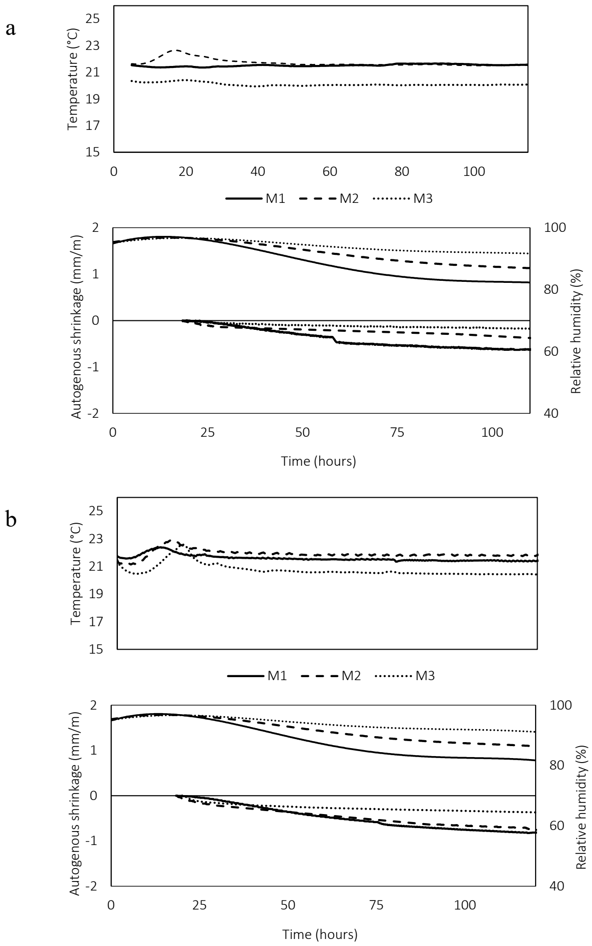

Fig. 4. Autogenous shrinkage measured as function of internal relative humidity change on: a) prism, b) tube specimens.

4 Conclusion

Shrinkage is a growing concern in high and ultra-high performance cementitious composites. A lower water content and higher cement content, together with mineral and chemical additives, lead to changes in the hydration process that result in altered volume deformation. The following conclusions can be drawn from the study presented in this paper:

- The replacement of cement with fly ash affects the early age properties of the hardened cement paste. The higher the proportion of fly ash in the binder, the lower the density and the longer the setting time of the mixture.

- The value of autogenous shrinkage depends strongly on time zero, i.e., the time during which the hardened cement paste develops a solid framework that allows the transfer of stresses.

- Fly ash affects the internal RH value during hydration; the higher the percentage of fly ash in the binder, the slower the internal RH value changes. This is evident in the slower self-desiccation of mixes containing fly ash.

- Considering that self-desiccation can still be observed after the final setting time, time zero is best described by a decrease in internal relative humidity.

- The values of autogenous shrinkage obtained for prisms are lower than for corrugated tubes. However, the same trend can be observed between the different test methods.

From the results obtained, it is clear that the determination of 'time zero' is of great importance. A future goal is therefore to investigate the relationship between different measurements of matrix formation, i.e. Vicat needle, electrical resistance or ultrasound, in order to determine more precisely the setting time as well as the relationship between autogenous and chemical shrinkage. In addition, the kinetics and extent of the cement hydration reaction, as determined by isothermal calorimetry, and the size and distribution of pores will also be investigated.

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