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Examining the “time-zero” of autogenous shrinkage in high/ultra-high performance cement pastes

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Keywords: Autogenous shrinkage; internal relative humidity; “time-zero”; Numerical simulation; high (ultra-high) performance cement paste

Abstract:

The term “Time-zero”, i.e., the time for the start of autogenous shrinkage measurement, is usually used for estimating the cracking potential of structural components. Accurate determination of the “time-zero” is therefore critical for autogenous shrinkage measurement, which is the main objective of this study.

There is a general agreement about the existence of a relationship between autogenous shrinkage and RH changes in hardening cement paste. An improved hygrometer method was developed for monitoring the change of internal RH in cement pastes 1 h after casting. This provides immediate experimental results of RH change for determining the “time-zero”. It indicates that the internal RH of cement pastes does not decrease immediately after the final setting time. A new “time-zero” is defined as the onset of internal RH drop, which is more reasonable for estimating the cracking potential of cement-based materials, compared to the “time-zero” represented by the final setting time.

1 Introduction

Ultra-high performance concrete (UHPC) and high performance concrete (HPC) show excellent performance regarding ductility, compressive strength and durability [1]. However, UHPC/HPC can experience large shrinkage deformation. A very high autogenous shrinkage occurs in the first one or two days after casting, which points to a considerable cracking potential at early ages [2,3]. Such early age cracking due to restrained autogenous shrinkage tends to negate the numerous advantageous properties of HPC and UHPC and significantly limits their prospective utilization in construction. The high autogenous shrinkage of these concretes is due to the low water-binder ratio and high amount of silica fume used which causes a significant drop in internal relative humidity (RH) in the cement paste during hardening, and self-desiccation occurs in absence of an external source of water [4]. Autogenous shrinkage and self-desiccation of concrete are known since the year 1900 [5], but their practical importance has only been recognized in last two decades. Although the actual driving force of autogenous shrinkage is still unclear [6], there is a general agreement about the existence of a relationship between autogenous shrinkage and RH changes in hardening cement paste [7,8].

When cement paste is in liquid state, the chemical shrinkage due to cement hydration is fully transformed into external volume change [7]. This volume change does not induce any cracking potential inside the material [9,10]. With the hydration of cement, a “stable” solid skeleton is formed in the hardening paste. Since then, in sealed condition, the chemical shrinkage cannot be totally transformed into external volume change. Empty pores are thus formed inside the paste and air-water menisci occur [11]. As the water is consumed by cement hydration, bigger pores inside the solid skeleton empty first [7]. This process is known as self-desiccation, in which the relative humidity drops.

“Time-zero”, corresponding to the start of autogenous shrinkage, is defined as the time when the cement paste develops a “stable” solid skeleton to enable tensile stress transfer [9]. Accurate determination of the “time-zero” is therefore critical for autogenous shrinkage measurement. The ASTM C1698-09 [12] establishes a set of standard methods to determine autogenous shrinkage and suggests to use the final setting time determined by Vicat apparatus as the “time-zero”. Due to the relative arbitrariness of the Vicat penetration method, some researchers [13-16] has questioned the reliability of using the final setting time as the “time-zero” for autogenous shrinkage. They believe that the penetration method does not precisely correspond to the “time-zero”. Bentur [13] found the “time-zero” is roughly equal but not identical to the final setting time. Miao et al. [14] illustrated the difficulty in measuring the moisture change in very early age concrete by conventional hygrometer method as the material is still in the super hygroscopic range (approximately in the range of 98%-100% of internal RH). They have developed a special measurement system for the meniscus depression within the paste or concrete, and determined the “time-zero” from the observed capillary depression [14]. Darquennes et al. [15] found the evolution of autogenous deformation strongly depends on the definition of the “time-zero”. Based on the free deformation curve tested in their research, three different definitions of the “time-zero” were considered: the initial or final setting time, the time of peak expansion at early ages, and the time characterized by the second maximal absolute value of the deformation rate (Fig. 1). The last definition was chosen as the “time-zero”, corresponding to development of significant stresses inside the specimen, and confirmed by Temperature Stress Testing Machine (TSTM). Miao et al. [14] tried to determine the “time-zero” of autogenous shrinkage by capturing the initiation of self-desiccation, and Darquennes et al. [15] tried to determine the “time-zero” as the time

for the initiation of internal tensile stresses. Because the self-desiccation is the main reason for the autogenous shrinkage [7], the “time-zero” determined by these two methods should be correlative. In this study, the “time-zero” is determined through analyzing the moisture change (internal RH change) at very early ages, and compared with the “time-zero” determined by Darquennes et al. [15].

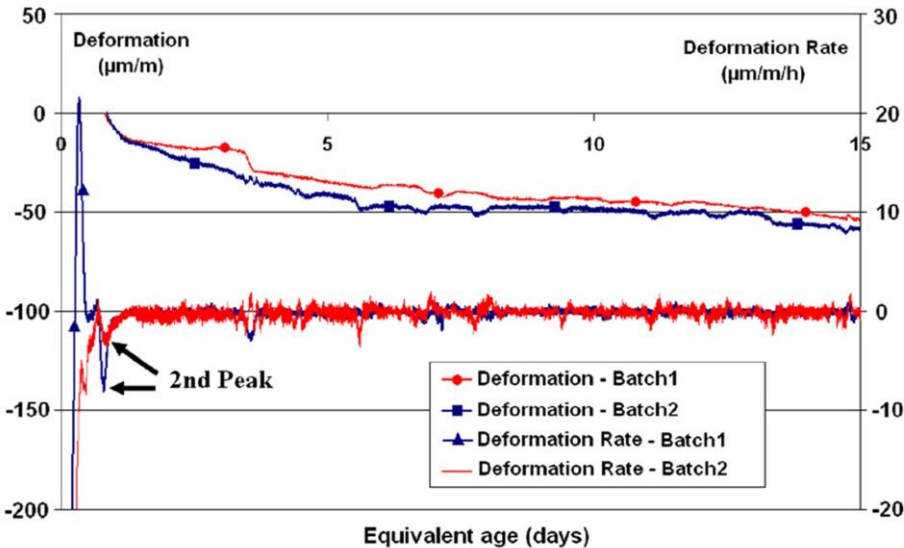


Fig.1. Evolution of the deformation rate and the autogenous deformation expressed from the second maximal value of the deformation rate of the CEM I mix. (Darquennes et al. [15]).

The typical procedure for measurement of internal RH is to place the cement paste in a small, sealed and thermostatic container. The internal RH of the cement paste is assumed to be equilibrated with the RH of the air inside the container, which in turn is measured by a humidity sensor [7]. In practical terms, 100% internal RH is easily reached at a very early age after casting, that is to say, up to several hours after mixing. According to Raoult’s law, the presence of ions in solution decreases the saturated vapor pressure of solution [6]. So, it is not possible that the internal RH of the pore solution in cement paste reaches 100% due to the effect of ions in the pore solution. Meanwhile, the internal RH is extremely influenced by the temperature. According to the Bulletin of the American Meteorological Society [17], when RH is above 50%, every 1°C difference in the dew point and dry bulb temperatures, the relative humidity decreases by 5%, starting with RH = 100% when the dew point equals to the dry bulb temperature. It means that, in high RH environments, water vapor is very easy to condense (RH=100%) on the surface of the colder object. Assuming that the internal RH of cement pastes is 98% in first several hours after mixing (which is also observed in experiments in this study); condensation can happen on the humidity sensor when the temperature of the humidity sensor is 0.4 °C lower than the water vapor. This makes the measurement of RH at very early ages very complicated. Especially if the hydration heat of cement is taken into account, the probability of condensation is even more.

Ultrasonic pulse velocity (UPV) measurement can be used for monitoring the development of solid skeleton inside cement paste. The UPV technique is based on a pulse generating and transmitting transducer and a receiving transducer. When cement paste is subjected to a pulse

vibration load, the longitudinal pulse transmitted to the paste is reflected at various solid-liquids interfaces or passes through the solid phase until it reaches the receiving transducer. With the development of cement hydration, the connection of smaller cement particles leads to clusters that form a solid skeleton. The UPV increases with the development of this solid skeleton, as the stiffness of the cement paste largely depends on the connection of the solid phase [18].

The main aim of this paper is to determine the accurate “time-zero” of autogenous shrinkage in HPC/UHPC. For revealing the autogenous shrinkage mechanism, the internal RH was monitored by improved hygrometer method at very early age (here refers to the stage before the final setting). Autogenous shrinkage of cement pastes was measured following ASTM C1698-09 [12]. For monitoring the stiffness development and hydration process of cement paste, ultrasonic pulse velocity measurement and isothermal calorimetry were performed.

2 Experimental investigation

2.1 Materials

The materials used in this study were Portland cement (CEM I 52.5N), and a polycarboxylate-based superplasticizer (Glenium 51, Solid mass content 35%). The properties of cement are shown in Table 1. The mineral composition of cement was calculated by the modified Bogue equation [19] as presented in Table 2. The particle size distribution of cement is shown in Table 3.

Table 1 Properties of cement

Components	Cement ^a
Chemical properties, % by weight	
CaO	64.0
SiO ₂	24.0
Al ₂ O ₃	5.0
Fe ₂ O ₃	3.0
SO ₃	2.4
Na ₂ O	0.3
K ₂ O	-
Loss on ignition (LOI)	1.3

^a Data provided from the company

Table 2 The mineral composition of cement CEM I 52.5N, % by weight (calculated by the modified Bogue equation [19]).

Compound	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Weight (%)	63.77	9.24	8.18	9.13

Table 3 Particle size distribution of cement.

Cumulative passing, % by volume	Particle size, μm
0	0.14
10	1.95
20	4.26
30	6.58
40	9.47
50	12.93
60	16.98
70	22.18
80	29.12
90	41.25
100	59.17

Four types of cement paste mixtures were made. The mixture proportion is listed in Table 4.

Table 4 Mixture proportion of cement pastes

	Water-cement ratio, by weight	Superplasticizer-cement ratio, by weight
Ref 0.28	0.28	0
Ref 0.28 SP	0.28	0.4%
Ref 0.25 SP	0.25	1.6%
Ref 0.18 SP	0.18	2.6%

2.2 Methods

2.2.1 Autogenous deformation test

The autogenous deformation of mixtures was measured following ASTM C1698-09 [12] standard developed by Jensen and Hansen [20], in which three sealed corrugated moulds of 440 mm ($\varnothing 28.5$ mm) were tested for each mixture. After mixing, the fresh paste was carefully filled into the corrugated tube and sealed by plug and sealing glue. The specimens and test instrument were immersed in glycol in a box where the temperature was regulated at 20 ± 0.1 °C with the help of water bath. The autogenous shrinkage of specimens was recorded every 5 min by linear variable differential transformers (LVDTs). Fig. 2 shows the autogenous shrinkage test system. In all the tests, the autogenous deformation of parallel samples had a similar trend with a deviation of less than 50 microstrains.

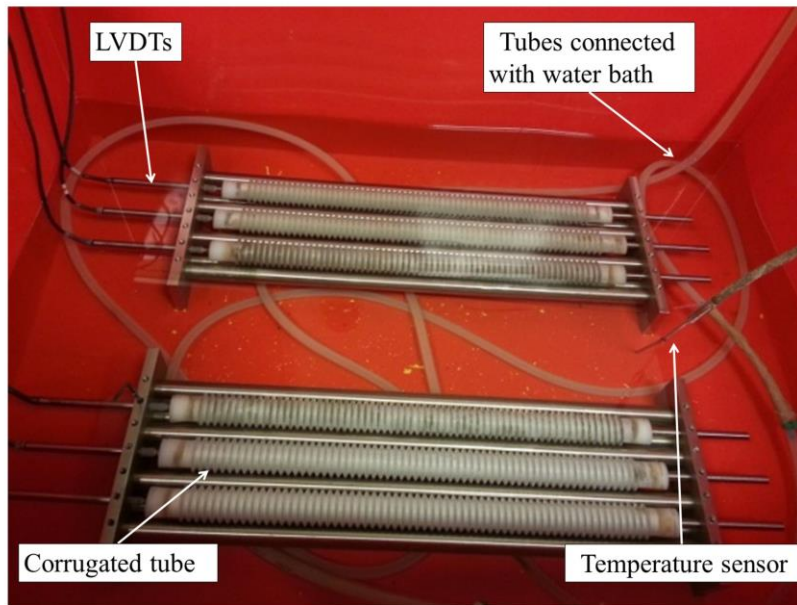


Fig. 2. Autogenous deformation measurement.

2.2.2 Internal RH measurement

The internal RH inside the cement paste was monitored by two Rotronic hygroscopic DT station equipped with HC2-AW measuring cells, which is the same test method used by Jensen [21]. The dimension of the sample container is 30 mm, the thickness of sample for the test is less than 7 mm, and the distance between sample and humidity sensor is less than 30 mm.

In order to avoid condensation on the humidity sensor in the very early stage (within one hour after mixing), a test procedure of internal RH measurement is developed and shown in Fig. 3. The specimen was sealed in sample holder by a sealing plug and put in test room with a temperature of 20 °C for 0.5 h to achieve temperature equilibrium after mixing (Fig. 3b). The sample holder was kept in a tightly sealed condition in order to prevent moisture loss. Considering the temperature of water vapor from cement pastes is a little higher than the pastes due to hydration heat of cement, the temperature of the water bath is set to 19.0 - 19.5 °C (depending on the efficiency of the water bath) for lowering the temperature of the cement pastes. Afterwards the sealed sample and the sample holder were placed in the water bath for at least 0.5 h to achieve temperature equilibrium (Fig. 3c). Then the sealing plug was replaced by the humidity sensor to start the test (Fig. 3d). The humidity sensor was kept in a climate chamber at a slightly higher temperature (for example, 20.3 °C) prior to the test for avoiding vapor condensation at the initial time. The total time for the preparation before the test is about 1 h. During the test, the humidity sensor was placed above the water bath, and the sample holder was immersed in the water bath. The environment temperature surrounding the humidity sensor was kept precisely at 20 ± 0.1 °C in a test room, so that the temperature of the humidity sensor be always higher than that of the pre-cooling pastes in the sample holder. The temperature change of the humidity sensor is less than 0.1 °C during the whole test (Fig. 4). In this way, the internal RH changes can be captured from the first hour after mixing, which was very hard to be obtained at early ages in previous test method [21]. The internal RH in the specimen and the temperature of water vapor were continuously measured (every 3 min) for a period of 1 week after mixing. Two parallel samples were measured for each

mixture. A similar trend was observed in the internal RH of all parallel samples. The deviation of tested value was less than 0.5%. The results are therefore presented as the average value of two parallel samples for each mixture. The RH sensors were calibrated by three saturated salt solutions in the range of 65-95% RH before and after every test. According to the calibration, the maximum measurement error of the RH sensors was $\pm 0.5\%$.

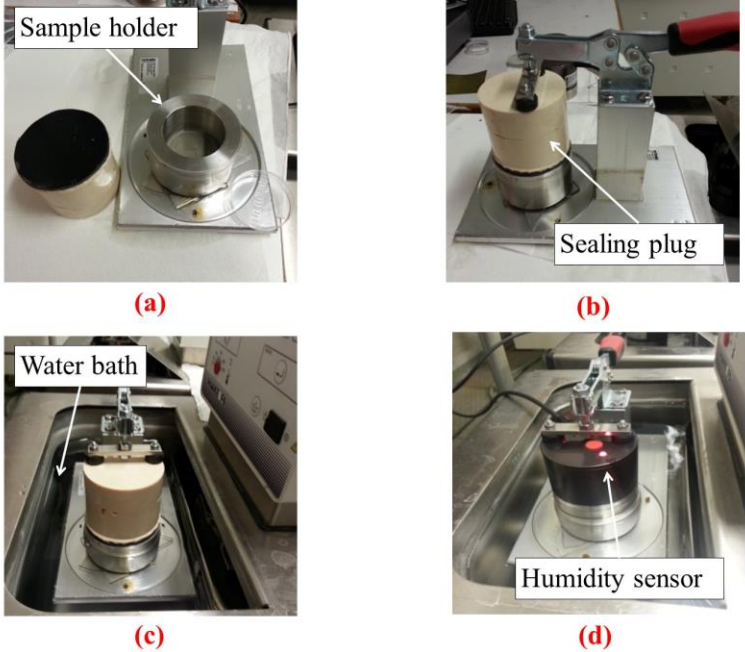


Fig. 3. Internal relative humidity test procedure. (a) Casting in the sample holder; (b) sealing the sample holder and curing in test room with temperature of 20 °C for 0.5 h; (c) placing the sample holder in the water bath for at least 0.5 h; (d) placing the humidity sensor (with slightly higher temperature (20.3 °C)) on the sample holder.

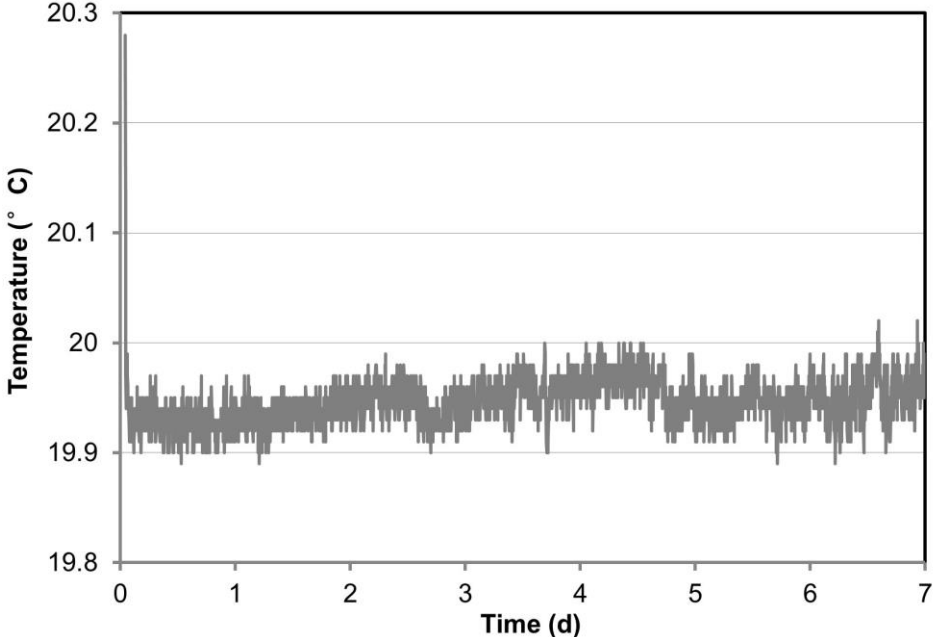


Fig. 4. The change of humidity sensor's temperature in the internal RH test.

2.2.3 Setting time measurement

Final setting time of sealed specimens was determined by Vicat apparatus (penetration method) according to the procedure described in standard EN 196-3 [22]. The diameter of upper surface of the sample was 70 ± 1 mm, the diameter of bottom surface was 80 ± 1 mm, the height of the sample was 40 ± 0.2 mm. The final setting test was operated manually. After each penetration test, the sample with mould was sealed in a plastic bag and stored in a chamber at 20 ± 0.1 °C for the next test. One sample was measured for each mixture.

2.2.4 Ultrasonic pulse velocity measurement

The ultrasonic pulse velocity measurement was conducted by means of portable ultrasonic non-destructive digital indicating tester. The ultrasonic transducers were integrated into a $150 \times 150 \times 200$ mm³ steel mould. The frequency of the transducers was 54 kHz. A software controlled the experiment and automatically recorded the time and the ultrasonic pulse transition time every 2 min for a period of 5 days. The whole system is regulated in temperature at 20 ± 0.1 °C using a cooling steel jacket. Two parallel samples were measured for each mixture. The test setup and test procedure are referred to [23].

2.2.5 Heat evolution

The rate of heat evolution of cement paste was measured with an isothermal conduction calorimetry at 20 °C for a period of 5 days. Three parallel samples were measured for each mixture. The test procedure was followed according to the test method proposed by CEN [24].

2.2.6 Mixing procedure

The mixing procedure followed the instruction given in ASTM C305-14. Autogenous shrinkage test, internal RH test and setting time test, were performed on the same batch of cement pastes.

3 Results and discussion

3.1 Free strain and internal RH change

The measured free strain of the mixture (Ref 0.28) is shown in Fig. 5. The deformation was recorded starting 1 h after mixing, and the strain was zeroed at the final setting time ($t = 2.97$ h) which was measured by Vicat apparatus. Based on the test result in Fig. 5, the deformation rate of the free strain of mixture - Ref 0.28 is calculated to compare with the internal relative humidity (RH) of cement paste in Fig. 6.

Fig. 5 shows that a significant part (more than 50%) of autogenous shrinkage (calculated since final setting time) of the mixture (Ref 0.28) in the first 7 days occurred within the first 12 h after casting. As shown in Fig. 5, a distinct “knee” on the autogenous shrinkage curve is found. The deviation of the results and the “knee” point between the three parallel samples was negligible. After this knee, the slope of the free strain curve has obviously changed. This trend is illustrated more clearly in Fig. 6. After the second maximal absolute value (2nd peak) of the deformation rate, the deformation rate decreases to nearly zero fluctuating within a narrow range between ± 50 ($\mu\text{m}/\text{m}/\text{h}$) in later ages. A similar experimental phenomenon was also observed by Darquennes et al. [15].

In Fig. 5, the intersection point between the deformation curve and X axis represents the final setting time ($t = 2.97$ h) of the mixture (Ref 0.28). It can be found that the slope of

deformation curve has not clearly changed at this final setting point.

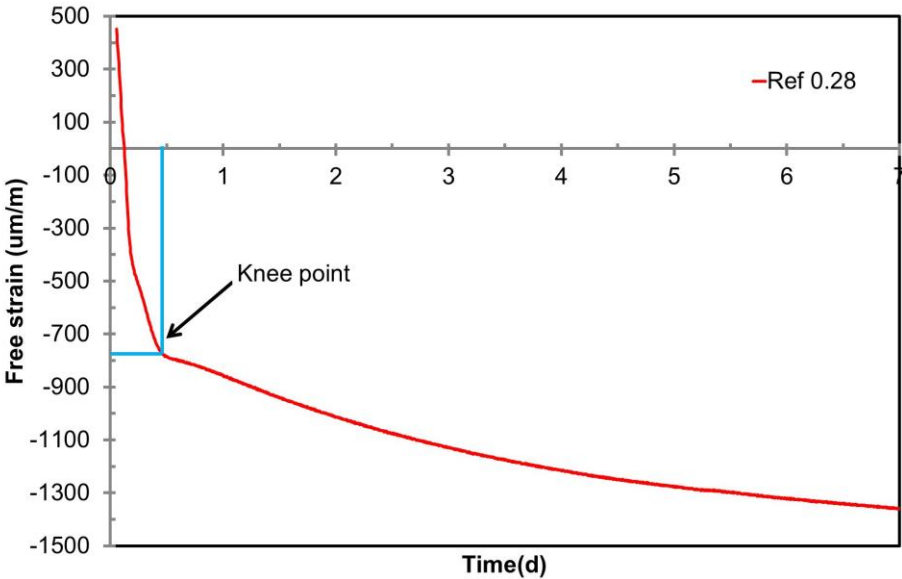


Fig. 5. Free strain measured on the mixture (Ref 0.28) after casting. (The strain is zeroed at the final setting time, $t = 2.97$ h).

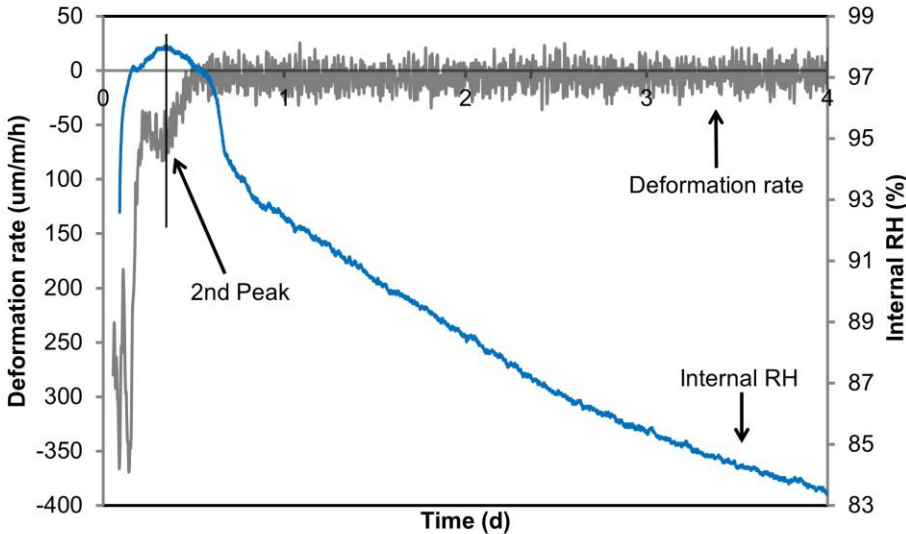


Fig. 6. Comparison between the deformation rate of the free strain and the internal RH in the mixture (Ref 0.28), measured after casting.

However, according to the definition of the “time-zero”, the final setting time which is chosen as “time-zero” in ASTM C1698, should represent the formation of a “stable” solid skeleton inside the cement paste. After the “time-zero”, the rigid skeleton is formed with enough stiffness, and the chemical shrinkage cannot be fully transformed into external volume change. It is expected that the slope of deformation curve, as shown in Fig. 5, has some changes due to the microstructure change around the final setting time. Nevertheless, this phenomenon is

not observed around the final setting time in Fig. 5, but a distinct “knee” at the 2nd peak of the deformation rate in Figs. 5 and 6. This indicates that “time-zero” at the final setting time determined by the penetration method may not reflect a real microstructure change inside the cement paste accurately.

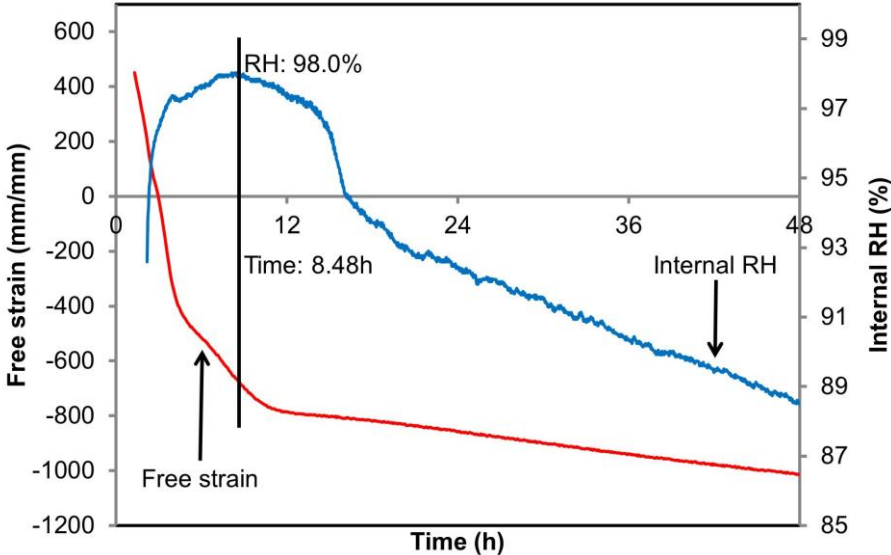


Fig. 7. Comparison between the free strain and the internal RH of the mixture – (Ref 0.28), measured after casting. (The strain is zeroed at the final setting time, $t = 2.97$ h).

The precise internal RH measurement (without condensation) records the internal RH when the pastes are still in the super hygroscopic range (approximately in the range of 98%-100% of internal RH). This provides immediate experimental data to discuss the “time-zero” of autogenous shrinkage caused by self-desiccation. As it can be seen in Fig. 6, the onset of the internal RH decrease, is almost corresponding to the 2nd peak of deformation rate of free strain. According to Darquennes et al. [15], this 2nd peak represents the initial time of internal tensile stress. The comparison of RH and deformation rate of free strain as shown in Fig. 6 proves the theoretical consistency between the start time of self-desiccation and the initial time of internal tensile stress.

Fig. 7 shows the comparison between the free strain and the internal RH of the mixture (Ref 0.28). It is noticed that the internal RH does not decrease until several hours after the final setting, but maintained at a high value. The internal RH starts to decrease at 8.48 h after casting, which is very close to the “knee point” on the free strain curve.

3.2 UPV and heat evolution

The result of ultrasonic pulse velocity measurement and the rate of the change of ultrasonic pulse velocity measurement of the mixture – (Ref 0.28) are shown in Fig. 8. The rate of heat evolution of the same mixture is also shown in Fig. 9a. The cement in this study is assumed to have a potential heat of hydration of 425 J/g calculated from [6]. Based on the cumulative heat evolution, the hydration degree of cement is shown in Fig. 9 b.

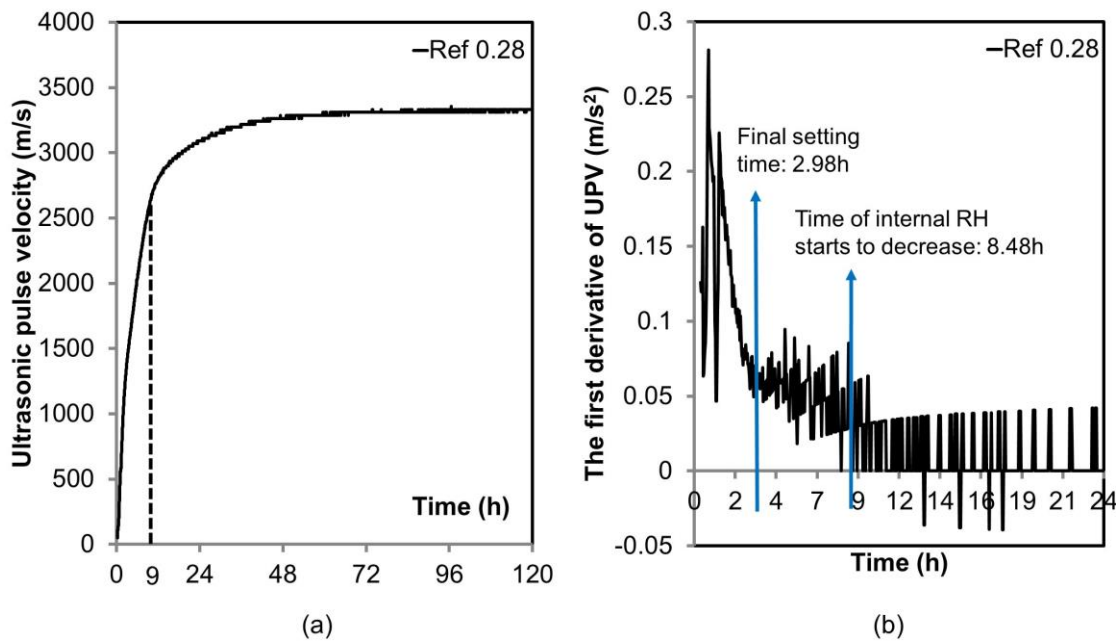


Fig. 8. (a) Ultrasonic pulse velocity measured on the mixture (Ref 0.28) for 120 h after casting; (b) the rate of change of ultrasonic pulse velocity measured on the mixture (Ref 0.28) for 24 h after casting.

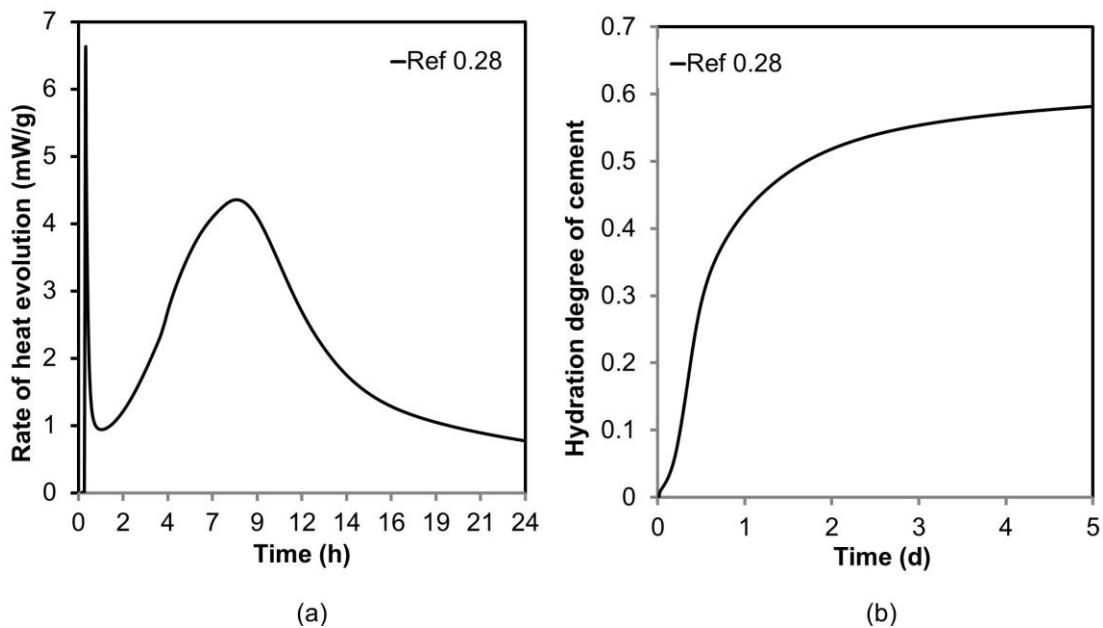


Fig. 9. (a) Rate of heat evolution measured on the mixture (Ref 0.28) in 24 h after casting; (b) hydration degree of cement in the mixture (Ref 0.28).

From Fig. 8 a, it is shown that UPV of the mixture (Ref 0.28) increases rapidly in the first 9 h after casting and then reaches a plateau. The rate of the change of UPV in the first 24 h after casting shown in Fig. 8 b provides a clearer view. The rate of the change of UPV slowly decreased until about 9 h after casting. After that, the rate of the change of UPV fluctuated

within a narrow range between ± 0.05 (m/s²), which corresponds to the plateau on the UPV curve. Due to the high influence of solid phase content on UPV at early ages of cement pastes [18], it illustrates that, after about 9 h of hydration of cement, a solid percolation path through the whole matrix has formed. After the formation of this solid percolation path, the newly-formed solid phase can still increase UPV by reducing the propagation distance of ultrasound waves going through the solid paths, but this effect is limited. This can be illustrated from the phenomenon that the rate of the change of UPV fluctuated within a narrow range after 9 h of hydration.

From the rate of heat evolution in Fig. 9b, it can be found that after 9 h of hydration, the hydration speed of cement decreased gradually. This indicates the generating speed of new hydration products also decreased after 9 h. On the one hand, the main solid skeleton has formed and newly-formed solid products have little effect on increasing the connectivity of solid skeleton after 9h as observed from UPV test. On the other hand, the generating speed of new hydration product is decreasing. These two factors both illustrate that, after a certain time of cement hydration, an integral solid skeleton has formed and will not change much its solid connectivity during the following hydration. At later hydration, this integral solid skeleton will be the origin of cement matrix stiffness, and sustain the pressure when the internal RH drops. However, whether this integral solid skeleton is the so-called “stable” solid skeleton, is not easy to determine with existing experimental tools. Therefore, cement hydration and microstructure modelling can be used as an alternative tool, for discussing the “stable” solid skeleton and the time when this “stable” solid skeleton forms.

3.3 HYMOSTRUC 3D modelling

The HYMOSTRUC 3D model [25,26,23] is developed to simulate the reaction process and the microstructure formation in hydrating Portland cement. In this model, the degree of hydration is simulated as a function of the particle size distribution and of the chemical composition of the cement, the water-cement ratio and the reaction temperature. With the help of HYMOSTRUC 3D, the microstructure development of cement pastes was simulated to discuss the “time-zero” determination.

The hydration process and the microstructural development of a $100 \times 100 \times 100 \mu\text{m}^3$ cubic sample of cement pastes were simulated. The water-cement ratio of the sample is 0.28, and the curing temperature is 20 °C. The simulated degree of hydration in HYMOSTRUC 3D was validated by the heat evolution measurement. From a statistic analysis, the size of $100 \times 100 \times 100 \mu\text{m}^3$ cubic sample of cement paste was proved to be sufficient to represent the volume element of a cement paste [27]. A “burning algorithm” [28] was employed to determine the connectivity of the cement matrix simulated by HYMOSTRUC 3D at different ages. This algorithm searches for a solid path across the 3D microstructure generated by HYMOSTRUC 3D. Firstly, the simulated 3D microstructure of cement paste is digitized with the information of solid phase and non-solid phase positions. Then, the burning algorithm proceeds iteratively from each solid phase to its nearest neighbors, and stops at the solid phase which has no other solid phase around. In this paper, the burning starts respectively at the top of the 3D microstructure in x, y, z directions and continues until no more 'fuel' remains. Then whether the bottoms in x, y, z directions have all been reached is checked, if so, i.e. the fraction of solids connected. The connectivity property of cement matrix at different time step from HYMOSTRUC 3D simulation is shown in Table 5. The 2D section images at the age of 3.16h and 8.91h are shown in Fig. 10 for the convenience of description.

Table 5 Connectivity of cement matrix at different time steps from HYMOSTRUC.

Time step	Hydration time (h)	Connectivity (Y/N)
1	1.00	N
...
10	2.82	N
11	3.16	N
...
19	7.94	N
20	8.91	Y
21	10.00	Y

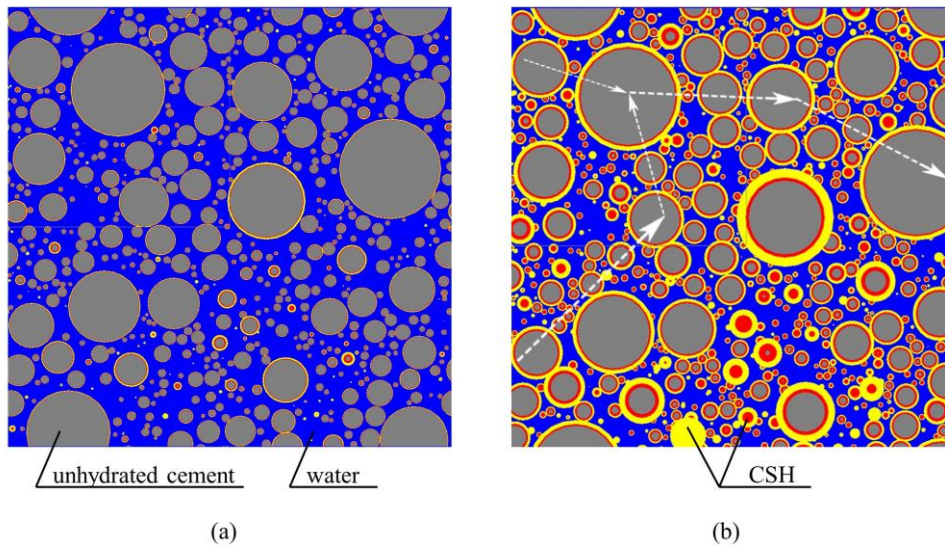


Fig. 10. 2D section images from HYMOSTRUC in the mixture (Ref 0.28) at different ages. (a) 3.16 h; (b) 8.91 h.

The connectivity of cement paste obtained from the simulation shows that there is an integral solid skeleton formed inside cement pastes between the hydration time at 7.94h and 8.91h, which is considered to be the “stable” solid skeleton in the discussion below. That means at the final setting time (2.98h), the degree of hydration is 0.03 (Fig. 9b), the system is more likely to be considered as a dispersion of solid phases in a liquid (Fig. 10a). At this time, the cement matrix is still in the plastic period, the internal stresses cannot be generated, and the chemical shrinkage can be transferred to the bulk volume change of the pastes. It is not proper to choose the final setting time as the “time-zero” for autogenous shrinkage when the “stable” skeleton inside the pastes has not formed. Only until the hydration time reaches 8.91 h, a “stable” solid skeleton, like in Fig. 10b, has formed in the model. The formation of the “stable” solid skeleton reflects the critical point of microstructure change. This point is corresponding to the knee point of the autogenous shrinkage curve (see Fig. 5).

3.4 New “time-zero”

The simulation result discussed above has a relatively good consistency with the result of UPV on the formation time of the “stable” skeleton. Both the UPV measurement and simulation result illustrate that the “stable” skeleton does not form at the final setting time. Whether the formation time of “stable” solid skeleton is the right “time-zero” will be discussed below.

When the “stable” solid skeleton is formed, empty pores could form inside the pastes due to the chemical shrinkage and air-water menisci appear [7]. When the air-water menisci form, the RH of pore solution begins to decrease, which is observed in Fig. 7. At the same time, the capillary tension coming from the air-water menisci starts to act on the solid skeleton, resulting in autogenous shrinkage. As the water is consumed by hydration, the Kelvin radius of menisci decreases continuously (Kelvin’s law); the solid skeleton sustains more and more capillary tensions [6]. This will lead to a considerable cracking potential when the specimen is restrained.

The formation of “stable” solid skeleton is a precondition for the RH drop [11], but it doesn’t mean that the RH must decrease right after the formation of the “stable” solid skeleton. For example, in the concretes with high water-cement ratios (w/c is more than 0.4-0.45) [7], when a “stable” solid skeleton has formed inside, the pores generated from chemical shrinkage are still full of free water. Therefore the RH does not drop at this time, and the autogenous shrinkage caused by self-desiccation is negligible. The high efficiency of internal curing on mitigating autogenous shrinkage by Super Absorbent Polymer (SAP) also proves that the autogenous shrinkage can be controlled by maintaining a high internal RH [29]. So, the formation time of “stable” solid skeleton does not represent the start of autogenous shrinkage in mixtures with high water-cement ratios or with internal curing agents. It’s therefore more reasonable to link the “time-zero” to the start of self-desiccation, i.e., the onset of internal RH drop as a new “time-zero”.

In order to capture the start point of self-desiccation more precisely, a curve fitting was performed during the transition period of internal RH curve by Bi-Gaussian Peak Function [30]. The coefficient of determination (R^2) of fitted curve is more than 0.98 in every mixture in this paper. The first derivative of the fitted curve was computed, and the time corresponding to the zero of the first derivative was chosen as the start time of self-desiccation, i.e., the new “time-zero”.

The comparison between free strain and internal RH of other three mixtures (Ref 0.25 SP, Ref 0.28 SP and Ref 0.18 SP) are shown in Figs. 11, 12, 13. It can be found that in all figures, the points on the free strain curves corresponding to the new “time-zero” are near or after the knee points of the autogenous shrinkage curves. The knee point reflects the threshold of solid percolation which is corresponding to the formation of the stable solid skeleton. Once the stable solid skeleton is formed, especially for cement pastes with a low water-cement ratio, the internal RH starts to decrease. Before the formation of the stable solid skeleton, the chemical shrinkage is the main reason of free shrinkage after casting. This has no harmful effect as the paste is still in the plastic period. However, as the internal RH drops, the internal stresses are generated on the solid skeleton, which increases the cracking potential of cement pastes.

Fig. 14 shows the autogenous shrinkage of cement mixtures with old “time-zero” (the final setting time) and new “time-zero” (the onset of internal RH drop). For each mixture shown in Fig. 14, the autogenous shrinkage using the old “time-zero”, is obviously higher than the one

using the new “time-zero”. As discussed above, as the chemical shrinkage was partly counted in the autogenous shrinkage when using the final setting time as “time-zero”, the autogenous shrinkage of cement mixture was overestimated. The new “time-zero” (the onset of internal RH drop) is therefore more reasonable for estimating the autogenous shrinkage caused by self-desiccation.

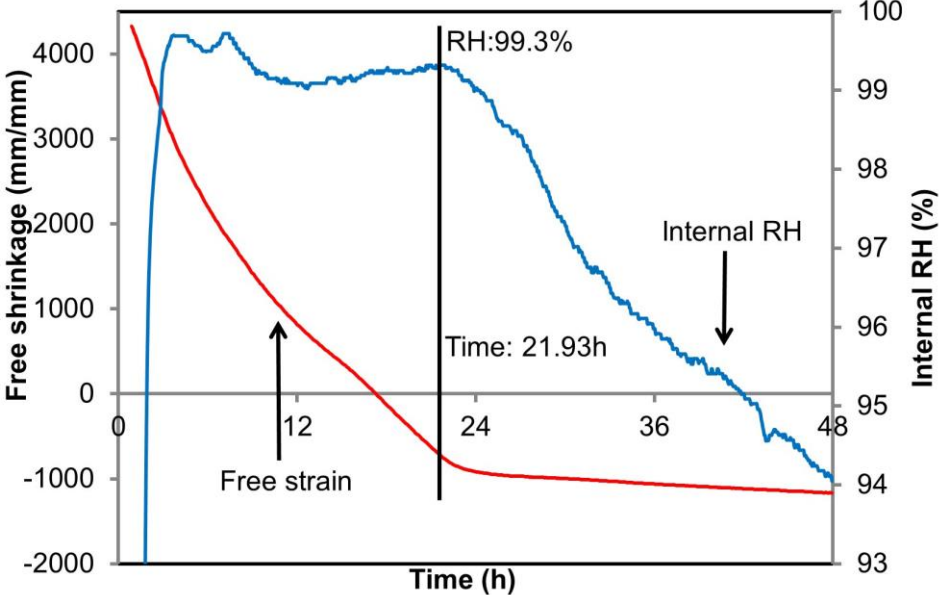


Fig. 11. Comparison between the free strain and the internal RH of the mixture (Ref 0.25 SP), measured after casting. (The strain is zeroed at the final setting time, $t = 17.28$ h).

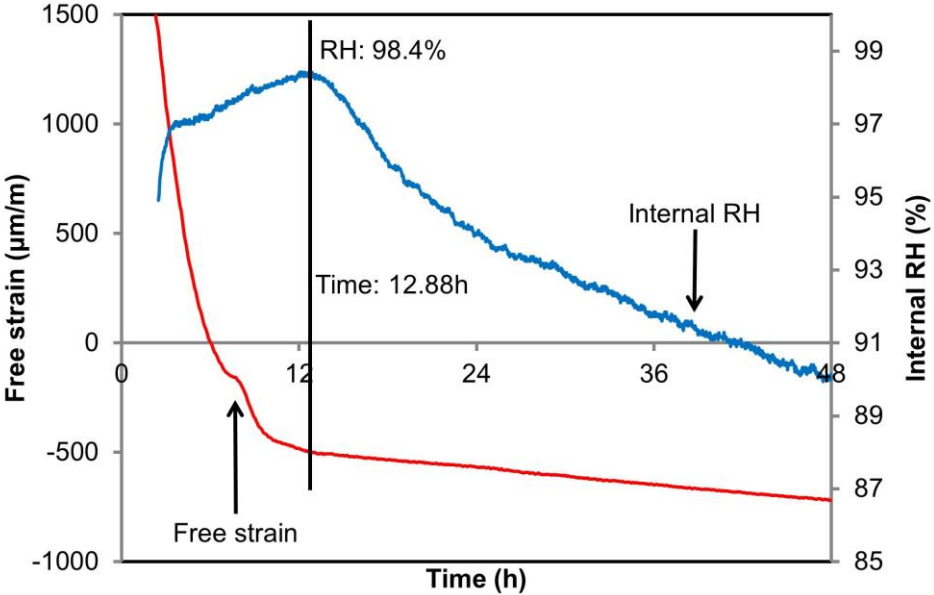


Fig. 12. Comparison between the free strain and the internal RH of the mixture (Ref 0.28 SP), measured after casting. (The strain is zeroed at the final setting time, $t = 6.02$ h).

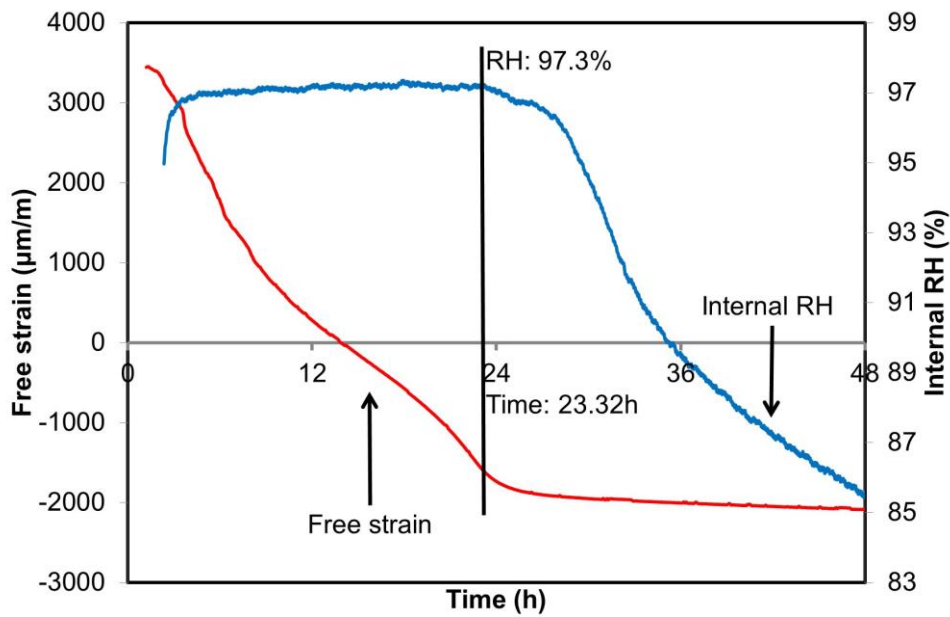


Fig. 13. Comparison between the free strain and the internal RH of the mixture (Ref 0.18 SP), measured after casting. (The strain is zeroed at the final setting time, $t = 13.87$ h).

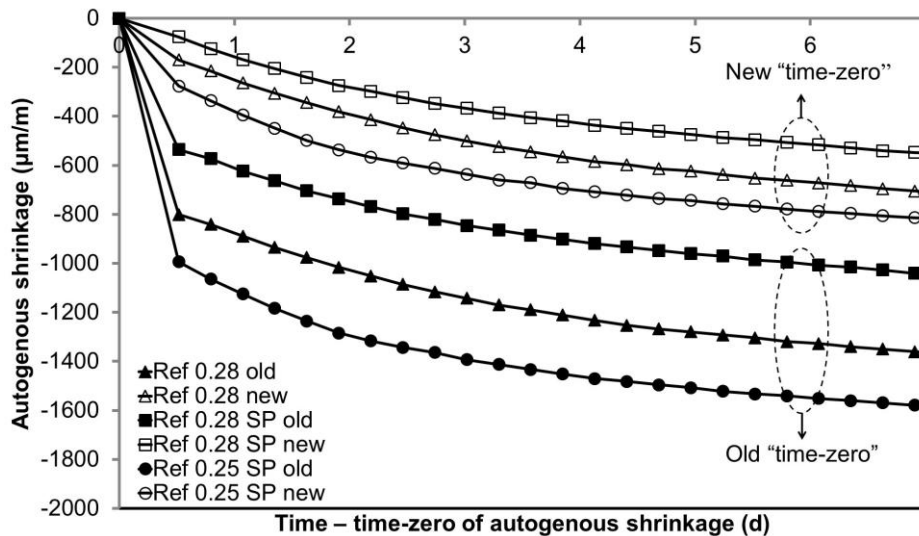


Fig. 14. Autogenous shrinkage of the cement mixtures with the old “time-zero” (the final setting time) and the new “time-zero” (the onset of internal RH drop).

4 Summary and conclusions

Accurate determination of the “time-zero” is critical for autogenous shrinkage measurement as a difference of one hour in the “time-zero” means several hundred microstrains. Therefore the autogenous shrinkage obtained from different “time-zeros” may provide totally different conclusions on estimating the cracking potential. In this study, the final setting time determined by Vicat needle test was proved to be an improper “time-zero”. This is because at the final setting time, the internal RH of cement pastes does not decrease and the “stable”

skeleton has not formed yet. Considering the formation time of “stable” solid skeleton as the “time-zero”, is also found inappropriate. In mixtures with high water-cement ratio or with internal curing agents, when a “stable” solid skeleton is formed inside the mixtures, the pores generated from chemical shrinkage are still full of free water. Therefore the RH does not drop and the autogenous shrinkage caused by self-desiccation is negligible. A new “time-zero” was proposed in this study with the help of improved hygrometer method. The new “time-zero” was directly linked to the start of self-desiccation, which is reflected in the drop of internal RH.

Based on the above discussions, the following conclusions can be made:

- Internal relative humidity of cement pastes does not decrease immediately after the final setting time determined by Vicat needle test.
- Both the UPV measurement and numerical simulation of cement pastes illustrate that the “stable” skeleton does not form at the final setting time.
- An improved hygrometer method was developed for monitoring the change of internal RH in cement pastes 1 h after casting.
- A new “time-zero” is defined as the onset of internal RH drop, which is more reasonable for estimating the cracking potential of cement-based materials, compared to the “time-zero” represented by the final setting time.

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