Autogenous shrinkage of zeolite cement pastes with low water-binder ratio

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Abstract

Self-desiccation is one common phenomenon of high-performance cementitious materials characterized by low water to cementitious material ratio (w/c). Autogenous shrinkage is closely related to the internal relative humidity (RH) drop and capillary pressure induced by self-desiccation in the cement pastes. However, there is debate about the determination of time-zero, the time at which autogenous shrinkage begins to develop.

The objective of this study is to provide an accurate determination of time-zero based on the relationship between the internal RH and autogenous shrinkage of low w/c ratio cement pastes. And according to the time-zero, cement pastes blended with zeolite were prepared to investigate the potential of zeolite as internal curing agent.

The autogenous shrinkage was conducted according to the standard method ASTM C1698. Internal RH was performed on the sealed cement pastes at very early age by conventional method of hygrometer. Setting time was determined by the Vicat needle apparatus according to the standard method ASTM C191.

Experimental results revealed that no internal RH drop was observed around the final setting time determined by the Vicat method. Besides, a knee point was observed in the shrinkage curve at the time when the internal RH began to decrease. This is the so-called time-zero. And zeolite was found to be a potential internal curing agent according to the autogenous shrinkage tests measured from the new time-zero.

Originality

There are many publications concerning the mitigation strategies for autogenous shrinkage of low w/b ratio cementitious materials, such as utilization of super absorbent polymer (SAP), lightweight aggregates (LWAs). However, both these two materials will result in negative influence on the mechanical properties of cementitious materials. Zeolite was proved to be a pozzolanic material, however few researches were carried out about the utilization of zeolite as internal curing agent in low w/c ratio cementitious materials. This study could present and explain the potential of zeolite for internal curing.

Keywords: autogenous shrinkage; relative humidity; time-zero; zeolite

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1. Introduction

(Ultra-) High performance concrete (HPC/UHPC) has become popular due to its excellent mechanical and durability properties. Typically, HPC/UHPC is characterized by low water/binder (w/b) ratio, high cement content and the incorporation of silica fume. All of these cause a significant drop in the internal relative humidity (RH) in the cement paste during hydration. It is the so-called self-desiccation, and will result in autogenous shrinkage, which increases the risk of cracking of concrete structures, especially at early ages (Persson B., 1997; Kim J.K. and Lee C.S., 1999). Autogenous shrinkage restrained internally by aggregates and externally by neighboring structural members will generate tensile stresses, which might cause cracking once the material strength is exceeded (Bentz D.P. *et al.*, 1997; Koenders E.A.B. and Van Breugel K., 1997). Hence, the mechanisms of autogenous shrinkage and the mitigation strategies for autogenous shrinkage is the main subject of research interest.

Although the mechanism of autogenous shrinkage is still under discussion, there is a general agreement about the existence of a relationship between autogenous shrinkage and internal RH changes in the pores of hardening cement paste. As long as the cement paste is fluid, the chemical shrinkage is totally converted into external volume change. When a solid skeleton forms in the hardening paste, the stiffness increases and gas bubbles start to nucleate and grow in the bigger pores due to the water consumption in the capillary pores. This leads to the formation of water-air menisci and the internal RH drops (Kelvin's law). The presence of menisci causes tensile stresses in the pore solution (Laplace's law) exerted on the solid skeleton, which leads to the autogenous shrinkage of cement paste (Jensen O.M. and Hansen P.F., 1996 and 2001a; Lura P. *et al.*, 2003).

One important problem involved in the research is how to reduce autogenous shrinkage of HPC or UHPC. Extensive studies on the mitigation strategies for autogenous shrinkage have been carried out, and internal curing by using appropriate curing agents, such as super absorbent polymer (SAP) (Jensen O.M. and Hansen P.F., 2001b and 2002), lightweight aggregates (LWAs) (Bentz D.P. and Snyder K.A., 1999; Bentur A. *et al.*, 2001), and wooden-derived materials (Mohr B.J. *et al.*, 2005), was experimentally proved capable to eliminate or considerably diminish autogenous shrinkage. These agents can absorb significant amounts of water either before or during mixing and release the water during concrete hardening. Normally, these agents are porous materials and will leave voids in the dense cement matrix (such as SAPs), resulting in negative influence on the mechanical properties of concrete. So, searching for proper internal curing agent remains the subject of research interest.

Zeolite was proved to be a pozzolanic material, which could improve the mechanical properties of concrete, however few researches were carried out about the utilization of zeolite as internal curing agent in low w/c ratio cementitious materials. B lek V. *et al.* (2002) used a pre-soaked fine zeolite powder (clinoptilolite type) to produce high performance concrete with low w/c, and found that 10% zeolite showed a small decrease in the autogenous shrinkage using the 1-day length as the reference. According to Zaichenko N.M. (2011), a fine zeolite aggregate (0.63-5 mm) reduced the autogenous shrinkage of the high performance concrete, but it induced higher drying shrinkage than the reference. Ghourchian S. *et al.* (2013) concluded that the natural zeolite (clinoptilolite type) aggregate is not a suitable agent for internal curing. Due to its fine pore structure, most of the absorbed water is retained even at 80% RH. As a result, the absorbed water is not available to counteract the self-desiccation and dry. The zeolite containing concrete shows a higher total shrinkage. But no information about the influence of zeolite on the autogenous shrinkage was mentioned in their studies. According to these studies, no common conclusion could be made. Therefore, the main motivation of this study was to investigate the potential utilization of zeolite as an internal curing agent for mitigating the autogenous shrinkage.

2. Experimental study

2.1 Materials

Cement pastes blended with or without zeolite were prepared with a low water to binder (w/b) ratio of 0.25. Portland cement (CEM I 52.5.N), 20 % zeolite (obtained from the Netherlands)

by mass of cement, and deionized water were used. The chemical and Bogue potential composition of the cement and chemical composition of zeolite are listed in Table 1. Figure 1 provides the particle size distribution of the cement and zeolite. The zeolite shows a finer particle size than the cement.

Tow mixtures were evaluated in this paper, a control cement paste and a zeolite blended cement paste. The mixture design is shown in Table 2. A polycarboxylate-based superplasticizer (Glenium 51, 35% SPL) was used to modify the fluidity of cement pastes.

Table 1 Chemical and Bogue composition of cement and zeolite (- not available or not applicable)

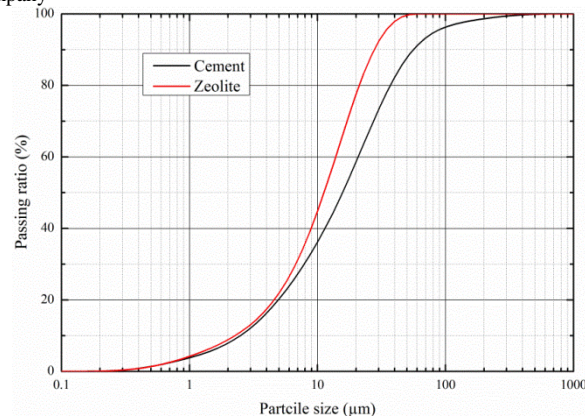| Material	Chemical composition/ % by weight								Bogue composition			
	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$	Na$_2$O	K$_2$O	L.O.I	C$_3$S	C$_2$S	C$_3$A	C$_4$AF
Cement*	64.0	24.0	5.0	3.0	2.4	0.3	-	1.3	63.77	9.24	8.18	9.13
Zeolite	10.01	55.00	15.94	6.95	0.19	-	9.26	-	-	-	-	-

* provided by the cement company

Figure 1 Particle size distribution of cement and zeolite

Table 2 Mixtures design (% by weight of cement)

Sample	Cement	Zeolite Replacement	w/b	Superplasticizer
Control	100	0	0.25	1.6
Z-20	80	20		1.0

2.2 Final Setting

Final setting of cement paste was determined using the Vicat needle test according to ASTM C 191-13 (2013).

2.3 Autogenous Shrinkage

Autogenous shrinkage of the paste was measured by the corrugated tube method, which was introduced by Jensen and Hansen (1995) and standardized as ASTM C1698-09 (2009). The technique is designed to minimize restraint of the paste, permitting measurements to start approximately 30 min after mixing. The fresh cement paste was casted into the corrugated tubes with a length of 420 mm and an outer diameter of 29 mm and vibrated. The specimens were maintained in a room at 20±1 ℃ on a dilatometer rig, which was equipped with linear variable differential transformer (LVDT) with a measuring accuracy of 2.5 μm/m. The autogenous shrinkage was measured by LVDTs and the data was recorded every 5 min automatically.

2.4 Internal Relative Humidity

The internal equilibrium relative humidity (RH) of hydrating cement paste was monitored by two Rotronic hygroscope stations equipped with WA-40TH cells. Each station was equipped with a Pt-100 temperature sensor and a DMS-100 H relative humidity sensor. During the measurement, the stations were immersed in water bath to maintain the temperature at 20±0.1 ℃. The stations were calibrated before measurement with standard salt solutions with known RH in the range 65-95% at 20 ℃. This gives a measurement accuracy of ±0.5 % in the absolute RH. More detailed information about the test procedure of the internal RH measurement can be found in the study of Huang H. and Ye G. (2014).

The cement paste was placed in the measuring cells of the RH stations after mixing and sealed by the sealing plug for about 1 hour. Afterwards, the sealing plug was replaced by humidity sensor. The RH in the specimen and the temperature in RH station was measured and recorded every 3 min automatically.

3. Results and Discussion

3.1 Autogenous shrinkage

The deformation was recorded from approximately 30 min after mixing. According to ASTM C1698-09 (2009), the autogenous shrinkage was zeroed at the final setting time. The final setting time of control and zeolite blended sample is 17.3 h and 7.7 h, respectively.

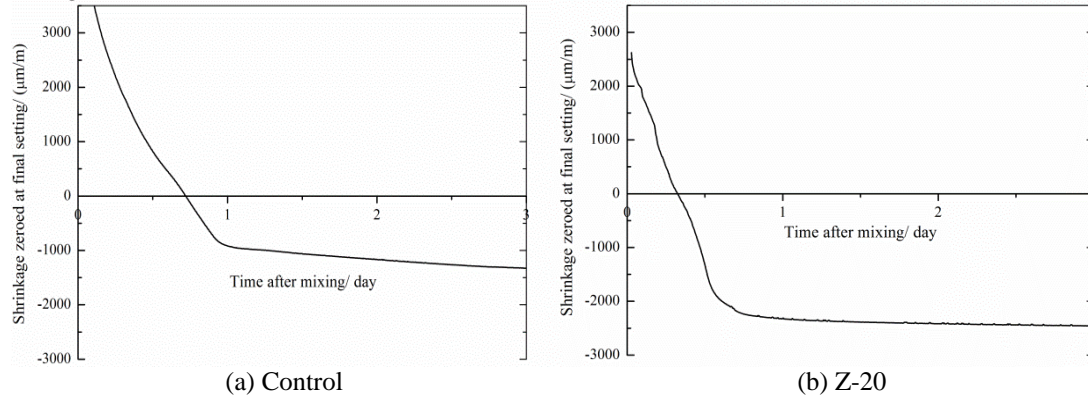(a) Control   (b) Z-20

Figure 2 Autogenous shrinkage zeroed to the final setting after mixing

Figure 2 shows the autogenous shrinkage zeroed to the final setting time as a function of time after mixing for the control and zeolite blended cement pastes. As shown in Figure 2(a), after mixing, the control sample underwent a monotonic quick shrinkage till several hours after final setting, after which the sample showed another continuous shrink but with a much slower rate. No significant change in the slope of deformation curve was observed at the final setting time. At 3 days after mixing, the autogenous shrinkage was 1325 μm/m, of which more than 50% occurred in the first several hours after final setting.

As shown in Figure 2(b), the zeolite blended sample also showed the similar trend in the change of the autogenous shrinkage curve. But it showed a much larger autogenous shrinkage at 3 days after mixing; it reached 2457 μm/m, and most part of it also occurred in the first several hours after final setting.

The results indicate that the addition of zeolite as a replacement of cement would lead to an increase of autogenous shrinkage if the autogenous shrinkage results are compared to those of control sample according to ASTM C1698-09 (2009).
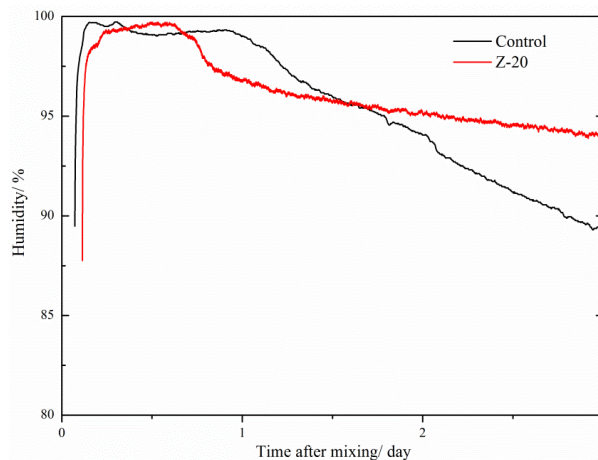
3.2 Relative humidity

Figure 3 Internal RH of cement pastes after mixing

The development of internal RH with time is provided in Figure 3. Both the control and zeolite blended sample showed a similar initial RH in the first several hours, about 99%. Due to the ions dissolution in the pore solution, the water activity is reduced and hence the internal

RH is lower than 100% in the initial stage. The initial RH value around 99% at the very early age was also reported on different cement pastes (Jensen O.M. and Hansen P.F., 1996; Chen H. *et al.*, 2013).

The very first sharp increase in RH was due to the disequilibrium between the humidity of RH sensor and the humidity of paste.

As shown in Figure 3, the internal RH of control sample stabilized at around 99% till 21.9 hours after mixing, and then it showed a monotonic decrease to 89.3% at 3 days after mixing. The internal RH of zeolite blended paste began to decrease at 14.3 hours after mixing. And several hours later, it was followed by a slower decreasing. At 3 days after mixing, the internal RH was 94.1%, which was higher than that of the control sample, indicating that the addition of zeolite as replacement of cement has a positive effect in the maintain of internal RH at high range. Due to its porous structure, the zeolite probably acts as an internal reservoir, providing a source of curing water to the paste in its vicinity.

3.3 Choice of "time-zero"

Chemical shrinkage begins with the contact of cement and water and it is totally converted into external volume change as long as the cement paste is fluid. When a solid skeleton forms in the hardening paste, chemical shrinkage can no longer be totally transformed into external volume change. And this time is the "time-zero", at which the self-supporting skeleton starts to develop and the stresses begin to develop.

One important problem involved in the research is the determination of "time-zero", i.e. the time for the start of autogenous shrinkage measurement. Deformations occurring before this "time-zero" can be ignored for stress calculation purposes, since they do not result in stresses. There is no general acceptance about the determination of this time, whether it corresponds to the initial setting, final setting, or some other time (Weiss J., 2006). This lack of standardization causes great difficulty in direct comparisons between results provided in the existing literatures.

As proposed by ASTM C1698-09 (2009), the final setting time is defined as the "time zero". However, it should be noted that the Vicat needle test is a mechanical method, whose result is largely depended on the consistency of the cement paste and thus on the water/binder ratio. If the Vicat test is used to determine "time-zero", different viscosities of the investigated pastes are unavoidable. What's more, according to the definition of the "time-zero", after the "time-zero", a solid stable skeleton in the hardening paste is formed, the chemical shrinkage can only be partly transformed into external volume change. So a decrease of the deformation rate is expected at the "time-zero". But, as shown in Figure 2, no change of the slope was observed at the final setting time in the deformation curves for both control and zeolite blended pastes. It is indicated that the final setting time does not act as the precise "time-zero". For the sealed cement paste, the water supply is restricted. After the "time-zero", the stiffness increases and gas bubbles start to nucleate and grow in the bigger pores due to the water consumption in the capillary pores. This leads to the formation of water-air menisci and the RH drops (Kelvin's law), referred to as self-desiccation. The increasing curvature of the menisci leads to the development of hydrostatic tensile stresses in the pore solution and compressive stresses exerted on the solid skeleton, which lead to the bulk deformation of the cement paste, called autogenous shrinkage (Jensen O.M. and Hansen P.F., 1996 and 2001a; Lura P. *et al.*, 2003). It is indicated that the autogenous shrinkage is part of the chemical shrinkage and is caused by the decrease of internal RH in pore structure. The solidification and the concurrent change of capillary pressure in the capillary pores start very slowly, and it is practically impossible to determine the precise onset of these processes. But the precise internal RH measurements of the pastes starting from the pastes are still in fluid phase supply reasonable experimental data to discuss the "time-zero" of autogenous shrinkage caused by self-desiccation. A systematic research about determining the "time-zero" in low w/b ratio cement pastes was carried out by Huang H. and Ye G. (2014), and they came to the conclusion that the "time-zero" could be link to the time when internal RH begins to drop.

Figure 4 displays the relation between the shrinkage and the internal RH of the cement pastes as function of time from mixing. In Figure 4, the shrinkage was zeroed at final setting. It can be seen that no internal RH drop was observed at around the final setting time for both the

control and zeolite blended pastes, but the internal RH began to drop several hours after final setting time.

As shown in Figure 4(a), the internal RH of control sample began to drop at 21.9 hours after mixing, corresponding to the knee point in the shrinkage curve. This time is the so-called new "time-zero". After the "time-zero", it developed a monotonic shrinkage at a much slower rate than that before the "time-zero", corresponding to the constant decrease of the internal RH. According to this new "time-zero", the autogenous shrinkage of control sample was 563 μm/m at 3 days after mixing (as shown in Figure 5).
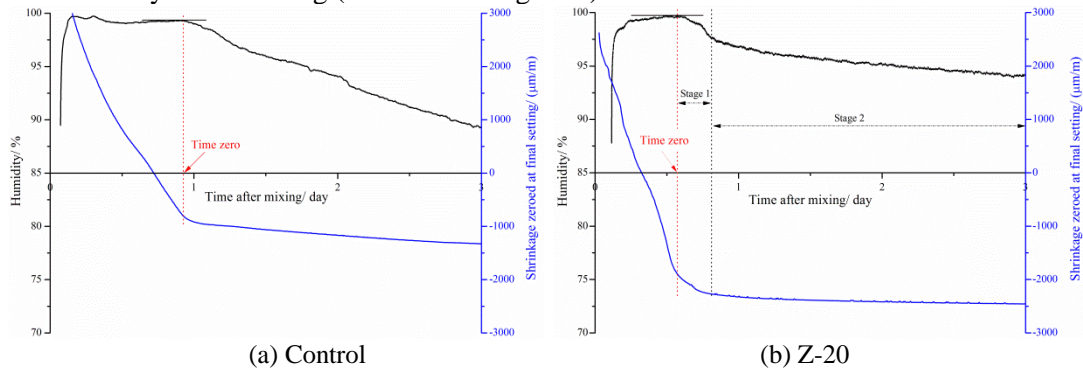

(a) Control   (b) Z-20

Figure 4 Relation between shrinkage and RH of mixtures as function of time after mixing

As shown in Figure 4(b), the internal RH of zeolite blended cement paste began to drop at 14.3 hours after mixing, and a knee point in the shrinkage curve was also observed. After the "time-zero", the internal RH curve showed a different characterization from that of control sample, which can be roughly divided into two stages. During the first few hours after the "time-zero", i.e. stage 1, a relative rapid decreasing of internal RH was observed. Then it was followed by a constant decreasing with a much slower rate at stage 2. As a porous material, the zeolite adsorbed part of the mixing water during the mixing process. As a result, the effective water to binder ratio was lower than 0.25 (the original total water to binder ratio) in the zeolite blended cement paste. According to the Kelvin equation, at a specific RH only the pore which is bigger than a proper size can be emptied, i.e. the size of 100 nm corresponds to internal RH in pores of roughly 99%. Because of the fine pore structure of zeolite, the adsorbed water in the pores can only start to be released slowly until the internal RH decrease to a relative low value. The lower effective water to binder ratio and the fact that the adsorbed water cannot be released result in the rapid decrease of internal RH during the first several hours (stage 1). Afterwards, the internal RH dropped to a relative low level, at which the adsorbed water start to be released out to act as internal curing water and it can help counteracting the effects of self-desiccation and slow down the decrease of internal RH. In the shrinkage curve, a significant shrinkage occurred during the period of the rapid decrease of internal RH at the stage 1; and then the curve tended to be almost flat corresponding to the period of slower decrease of internal RH (stage 2).
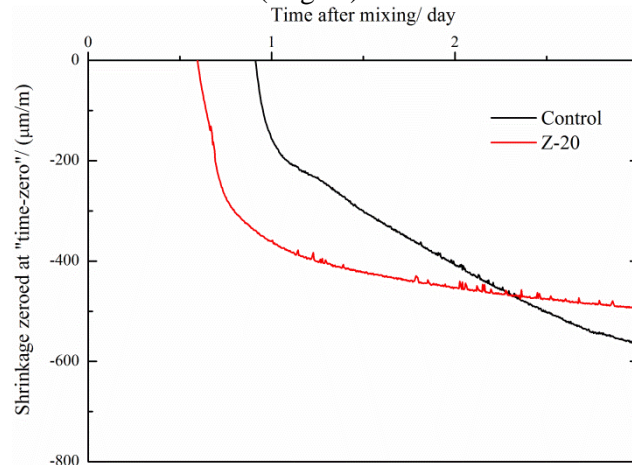

Figure 5 Shrinkage zeroed at the 'time-zero' defined by the onset of RH drop

The autogenous shrinkage zeroed at the "time-zero" defined by the onset of internal RH drop is illustrated in Figure 5. At 3 days after mixing, the autogenous shrinkage of Z-20 was 494 μm/m, which was slightly less than that of the control sample.

Considering the impact of zeolite on the internal RH and autogenous shrinkage of the paste, the zeolite shows a potential application as an internal curing agent. But it has to be noticed that, in the zeolite blended cement paste, the majority of the autogenous shrinkage occurred during the first several hours after "time-zero" as well as the rapid internal RH drop. Modification of the pore structure of zeolite should be performed to optimize the release mechanism of absorbed water from the pores during the hydration, aiming to diminish the rapid internal RH drop at the very beginning after "time-zero" and the autogenous shrinkage as well.

4. Conclusion

This paper accesses the early age autogenous shrinkage behavior of low w/b ratio cement paste blended by zeolite. Main findings can be made as follows.

(1) No internal RH drop was observed at the final setting time; the internal RH begins to decrease several hours later than the final setting time, corresponding to a knee point in the shrinkage curves.

(2) According to the "time-zero", the time when internal RH begins to drop, the cement paste blended by 20% zeolite shows a higher internal RH and a slightly less autogenous shrinkage than those of control sample at 3 days after mixing.

(3) The zeolite shows a potential application as an internal curing agent; modification of the pore structure of zeolite should be performed which might help diminish the rapid internal RH drop at the very beginning after "time-zero" and the autogenous shrinkage as well.

Acknowledgements

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