

Study on autogenous shrinkage characteristic and mechanism of ultra-high performance cementitious composite

Li Caixia¹, Sun Zhilin², Yang Liqi³ and Zhang Guorong^{4,5}

1 Zhangye municipal government and social capital cooperation management center office, Zhangye, China

2 Zhangye Traffic Construction Investment Co., Ltd., Zhangye, China

3 Chengde Road & Bridge Construction Corporation, Chengde, China

4 JSTI Group, Nanjing, China

5 State Key Laboratory of Safety and Health for In-service Long Span Bridges, Nanjing, China

Abstract. The self-designed vertical dial gauge holder was used in this paper. The influence factors of autogenous shrinkage of UHPCC, which include water-binder ratios, binder-aggregate ratios, sand ratios and fraction process of steel fiber, were mainly studied. The mechanism of autogenous shrinkage is explored by thermal analysis and pore structure analysis techniques. The results show that autogenous shrinkage of UHPCC increases with the decreasing of water-binder ratio. The autogenous shrinkage of 60d increases by 14.4% and 25.4%, when water-binder ratio decreases from 0.24 to 0.20, 0.16, respectively. Coarse aggregate has great positive effects on the autogenous shrinkage of UHPCC. Fine steel fibers have no obvious effects on the autogenous shrinkage of UHPCC. Non-evaporable water content decreases with the decreasing of water-binder ratio, which is positive effect on the autogenous shrinkage. However, the volume fraction of pores with the size range from 5 to 50 nm increases with the decreasing of water-binder ratio, which is negative effect on the autogenous shrinkage. Self-dessication effect is dominant factor in the autogenous shrinkage.

1. Introduction

Ultra-High Performance Cementitious Composites (UHPCC) is aimed at the problems of high cost, high energy consumption, complicated preparation process and difficult application in practical engineering for Reactive Powder Concrete (RPC) Using Portland cement and a variety of industrial waste as a matrix, with high strength coarse aggregate and short steel fibers as an enhancement to obtain a cement-based composite material with good flow properties, excellent mechanical properties and durability through the conventional preparation technology. Therefore, it has a wide range of application prospects in modern military protection projects as well as super high-rise, large span and some structural projects that have been subjected to dynamic loads for a long time.

Due to the low water-cement ratio of UHPCC, large amount of cementitious material, and the incorporation of superplasticizer, resulting in large autogenous shrinkage deformation, when the concrete is subject to internal or external constraints, it will produce tensile stress in concrete, it will emerge some cracks if the tensile stress beyond the tensile strength, the cracks will cause further significantly deteriorated influence to the mechanical properties and durability of cement-based



materials. At present, the research on autogenous shrinkage of cement-based materials mainly focuses on high-strength concrete^[1-4] and high-performance concrete^[5-9], and few studies on UHPCC have been conducted. The research on the autogenous shrinkage that caused by water-binder ratio^[10], steel fiber content^[11] has been done already. while fewer studies about sand rate, the ratio of binder-aggregate and other factors have been developed. Therefore, it is of great importance to study the self-shrinking properties of UHPCC and their related mechanisms systematically.

Vertical dial gauge holder method for the autogenous shrinkage (1d to 60d after molding) of ultra-high performance cementitious composites was used in this paper. The autogenous shrinkage properties of ultra-high performance cementitious composites were systematically discussed under the conditions of different water-cement ratios (0.16, 0.20 and 0.24), different ratios of binder-aggregate (1: 1, 1: 2 and 1: 3), different rates of sand (0.4, 0.5 and 0.6) different steel fiber volume contents (0%, 1%, 2% and 3%). Besides, the mechanism of autogenous shrinkage was explored by comprehensive thermal analysis, Mercury method and Micro-analysis technology.

2. Experimental Study

2.1 Raw Material.

Cement (C): P · II 52.5 Portland cement produced in Konan Onoda, Nanjing, with a density of 3100kg / m³; fly ash (FA): Class I fly ash produced by Jiangsu Nantong Power Plant, with a density of 2700kg / m³; Silica fume (SF): Elkem Shanghai Company, with a density of 2100kg / m³; Slag (SL): Nanjing Jiangnan Cement Co., Ltd. production S105 ground slag, with a density of 2870kg / m³; fine aggregate: ordinary river sand, the apparent density is 2650kg / m³; coarse aggregate: 5 ~ 10mm basalt crushed stone, the apparent density is 2950kg / m³; steel fiber: Steel fiber: Copper alloy superfine-plated steel fiber produced by Ganzhou Grand Industrial Co., Ltd., with diameter of 0.17mm and length of 15mm; Water-reducing agent: polycarboxylate superplasticizer produced by Jiangsu Su Bot company, 50% solids, water reduction rate of 40% or more.

The chemical composition and physical properties of the cementitious materials are shown in table 1.

Table 1. The chemical composition and physical properties of the cementitious materials

Binder	Chemical composition /%							Specific surface area /(m ² /kg)
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	IL	
C	16.52	8.33	3.37	69.52	0.85	1.53	1.59	310
FA	39.07	48.52	3.37	5.96	1.32	0.46	3.50	345
SF	95.01	0.82	1.86	0.35	1.24	0.32	1.58	20500
SL	32.07	14.68	0.97	35.81	9.30	2.51	0.58	480

2.2 Experiment Scheme.

A total of 16 UHPCCs were designed for autogenous shrinkage (from 1 day to 60 days after forming), of which W / B-0.16, W / B-0.20 and W / B-0.24 were used to study the effect of water- binder. B/A-1, B / A-2 and B / A-3 were used to study the effect of the ratio of binder- bone; SR-0.4, SR-0.5 and SR-0.6 were used to study the effect of sand rate; FB-0, FB-1, FB -2 and FB-3 were used to study the influence of volume fraction of steel fiber. The amount of superplasticizer was 2% of the amount of cementitious material. The specific mixing proportion is shown in table 2.

Table 2. Mixing proportion of UHPCC

No.	Water-binder ratio	Proportion of cemen-titious material (%)				Binder-aggregate ratio	Sand ratio	Volume fraction of steel fiber (%)	90d compressive strength(MPa)
		C	FA	SF	SL				

W/B-0.16	0.16	60	10	10	20	1:2	0.5	2	150
W/B-0.20	0.20	60	10	10	20	1:2	0.5	2	130
W/B-0.24	0.24	60	10	10	20	1:2	0.5	2	118
B/A-1	0.16	60	10	10	20	1:1	0.5	0	88
B/A-2	0.16	60	10	10	20	1:2	0.5	0	121
B/A-3	0.16	60	10	10	20	1:3	0.5	0	112
SR-0.4	0.16	60	10	10	20	1:2	0.4	0	112
SR-0.5	0.16	60	10	10	20	1:2	0.5	0	119
SR-0.6	0.16	60	10	10	20	1:2	0.6	0	122
FB-0	0.16	60	10	10	20	1:1	1	0	103
FB-1	0.16	60	10	10	20	1:1	1	1	132
FB-2	0.16	60	10	10	20	1:1	1	2	151
FB-3	0.16	60	10	10	20	1:1	1	3	175

In addition, three groups of water-cement ratio (0.16, 0.20 and 0.24), the hydration process and pore structure parameters of three mixed mineral admixtures (10% SF, 10% FA and 20% SL instead of cement) at 7d, 14d age cementitious composites were studied by means of comprehensive thermal analysis (DSC-TG) and mercury intrusion porosimetry (MIP) and further explored the autogenous shrinkage mechanism of ultra-high performance cement-based composites. The mixing proportions of three groups were shown in table 3.

Table 3. The experimental mixing proportions of DSC-TG, MIP

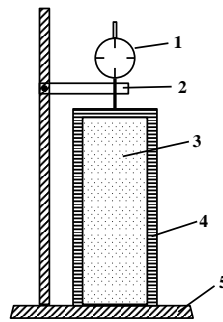
No.	water-binder ratio	Composition of cementitious materials (%)			
		C	SF	FA	SL
W/B-0.16	0.16	60	10	10	20
W/B-0.20	0.20	60	10	10	20
W/B-0.24	0.24	60	10	10	20

2.3 Test Methods.

2.3.1 Testing method of autogenous shrinking.

A self-designed vertical dial gauge holder device was used to test the autogenous shrinkage properties for UHPCC, shown in figure 1. One rack and chuck play a role in fixing the indicator and test pieces and ensuring full contact between them, the changes in the vertical length of cement-based composite materials were reflected through the changes in readings. For autogenous shrinkage test, to ensure the specimen and the surrounding environment has no moisture exchange is the most basic prerequisite, PVC pipe and plastic film was used to seal the test piece in this test.

autogenous shrinkage test specimens for ultra-high performance cement-based composites were prepared with a length of 400 mm and a diameter of 10 mm PVC pipe. Before the experiment, the organic sealant is used to bond the PVC pipe and the plywood. After the sealant is completely dried, the long-term autogenous shrinkage mold with the plywood as the bottom surface and the PVC pipe as the side surface is prepared. 1d after the specimen is molded, removing the bottom surface of the test pattern of the plywood, placing the specimen on the indicator frame, adjusting the height of the chuck, after the dial indicator is installed, starting the long-term autogenous shrinkage test, reading and recording corresponding age of the dial indicator value. Test environment temperature is 20 ± 2 °C, relative humidity is $60 \pm 5\%$.



1- Dial gauge; 2-Collet; 3-UHPCC; 4-PVC pipe; 5-Hob

Figure 1. Testing apparatus of autogenous shrinkage of UHPCC

2.3.2 Comprehensive thermal analysis.

Netzsch STA449 F3 Synchrotron Thermal Analyzer (DSC / DTA-TG) of Germany resistant company was used in this test. In this experiment, the heating rate of synchronous thermal analyzer is 10 °C / min and heated to 1000 °C to get the DSC-TG curve. The process of UHPCC sample preparation: The fresh cement slurry was put into the plastic sealed bags, in order to eliminate the bleeding of the slurry and stratification, every 10min the plastic sealed bag was inverted several times, removing the sealed bag after the final seal. The sample is placed in 20 °C fog chamber and maintained immediately. By the age of 7d and 14d, the appropriate amount of hardened paste was crushed, immersed in anhydrous ethanol to stop the hydration, ground in an agate mortar to pass through a 200 mesh sieve to produce the desired sample.

2.3.3 Pore structure analysis.

The pore structure parameters of UHPCC were measured by mercury intrusion porosimetry (MIP). Autopore IV9510 automatic mercury porosimeter was used. The measured pore size ranged from 3.6nm to 400um. The maximum pressure was 60000 psia (414MPa). Sample Preparation Process: When the specimen is cured to 7 days and 14 days, the test sample is cut into small pieces of about 10mm × 10mm × 10mm with a small cutting machine, put it into anhydrous ethanol to stop hydration and soak for 24h. After that, it is put into a vacuum drying oven with the temperature of 60 ± 2 °C to dry the sample.

3. Results and Analysis

3.1 Autogenous Shrinkage Characteristic of UHPCC

3.1.1 Effect of water-binder ratio

Under the same conditions of other parameters (the content of basalt coarse aggregate and steel fiber volume is 2%), the autogenous shrinkage characteristics of UHPCC with different water-cement ratios of 0.16, 0.20 and 0.24 were studied. The results are shown in figure 2. It can be found from the figure that the autogenous shrinkage characteristic shows a rapid growth in the early period and tend to be a steady growth in the late period. The three groups of 7d UHPCC autogenous shrinkage were 78.7% ($W/B = 0.16$), 59.7% ($W/B = 0.20$) and 60.2% ($W/B = 0.24$), the main reason is that the internal self-dessication effect is determined by the hydration reaction rate of the cementitious material. The early hydration reaction rapidly causes the internal free water to be consumed rapidly and the self-dessication effect also develops rapidly. As the age increases, the speed of hydration reaction decreases and tends to stabilize, the self-dessication effect also decreases and tends to stabilize.

At the same time, it can also be seen that with the decrease of water-cement ratio, the autogenous shrinkage value increased obviously. The autogenous shrinkage values at 60d were 365×10^{-6} ($W/B = 0.16$) and 333×10^{-6} ($W/B = 0.20$) and 291×10^{-6} ($W/B = 0.24$) respectively, and the autogenous shrinkage value of 60d increased by 14.4% and 25.4% respectively when the water-cement ratio decreased from 0.24 to 0.20 and 0.16 respectively. This is mainly affected by two factors: Firstly, the increase of water-cement ratio plays the role in thinning the pores, leading to an increase in capillary tension;

Secondly, with the water-cement ratio reduced, the internal free water decreases, with the hydration of cementitious material, material self-dessication occurs earlier in advance and with the water-cement ratio reduced the effect become more obvious.

3.1.2 Effect of binder-aggregate ratio

The the experimental of autogenous shrinkage characteristics were studied under the premise of keeping the water-cement ratio of 0.16 and the sand rate of 0.5 and the three groups of UHPCC are at different ratios of binder-aggregate (B / A-1: 1, B / A-1: 2 and B / A-1: 3), the test results were shown in figure 3.

It can be seen from the figure that UHPCC autogenous shrinkage also shows rapid growth in the early period and steady growth in the late period with the development of the age. At the same time, the volume fractions of the aggregates were 42.3%, 59.5% and 68.8% respectively when the ratios of binder-aggregate are 1:1, 1:2 and 1:3 respectively. The autogenous shrinkage values at 60d were 556×10^{-6} and 391×10^{-6} and 344×10^{-6} , 60d autogenous shrinkage value decreases with the decrease of the ratio of binder-aggregate. This is because aggregates are a fixed-volume component of concrete that play a skeletal role in cement-based composites and have an important limiting effect on shrinkage and deformation. Decreasing the binder-aggregate ratio indicates that with the increase of the aggregate volume fractions in the cementitious composites, the corresponding limit effect is even more significant. In addition, as the volume fraction of aggregates increases, the amount of cementitious material per unit volume decreases and the self-dessication shrinkage resulting from hydration of the cementitious material decreases.

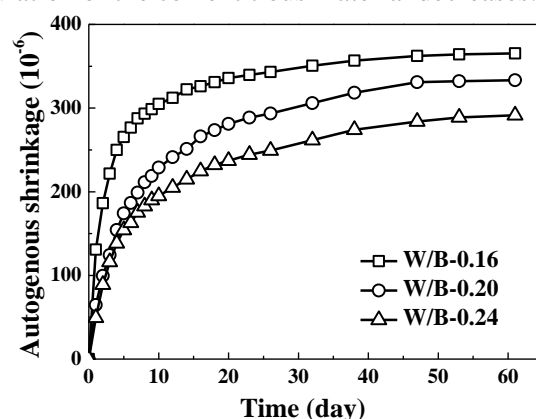


Figure 2. Effect of W/B

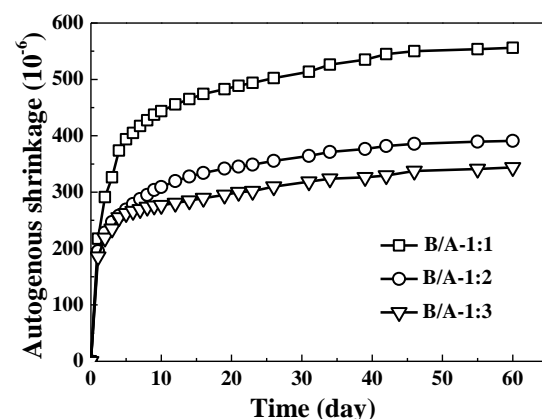


Figure 3. Effect of B/A

3.1.3 The impact of sand rate

Three different sets of sand rate (0.4, 0.5 and 0.6) UHPCC autogenous shrinkage characteristics were tested at binder-aggregate of 1:2. The results are shown in figure 4. The autogenous shrinkage increases with the increase of sand rate. The autogenous shrinkage values at 60d are 345×10^{-6} (SR = 0.4), 391×10^{-6} (SR = 0.5) and 440×10^{-6} (SR = 0.6), the autogenous shrinkage value of 60d increased by 13.3% and 15.9% respectively when the sand rate increased from 0.4 to 0.5 and 0.6. This is mainly due to the decrease of the overall elastic modulus of aggregates when the ratio of water-binder and the ratio of binder-aggregate are constant^[12,13], thus weakening the skeleton effect of aggregates and the restraint effect of the shrinkage and deformation for cementitious composites is also weakened.

3.1.4 The influence of steel fiber volume

The autogenous shrinkage tests were carried out on UHPCC (non-aggregated volume) with water-cement ratio of 0.16 and steel fiber volume contents of 0%, 1%, 2% and 3% , the long-term autogenous shrinkage effect was also studied, the results were shown in figure 5. It can be seen from

the figure that with the increase of steel fiber volume fraction, the UHPCC decreased slightly from long-term autogenous shrinkage. The autogenous shrinkage values at 60d were 670×10^{-6} (FB-0%), The volume fraction of steel fiber increased from 0% to 1%, and the volume fraction of steel fiber increased from 0% to 1%, and the volume of steel fiber increased from 1% to 647×10^{-6} FB-1%, 629×110^{-6} FB-2% and 606×10^{-6} FB- % And 3% respectively, the autogenous shrinkage value at 60d decreased 3.4%, 6.1% and 9.6% respectively. The short-steel steel makes no difference to UHPCC after 1d molded for its long-term autogenous shrinkage inhibition effect.

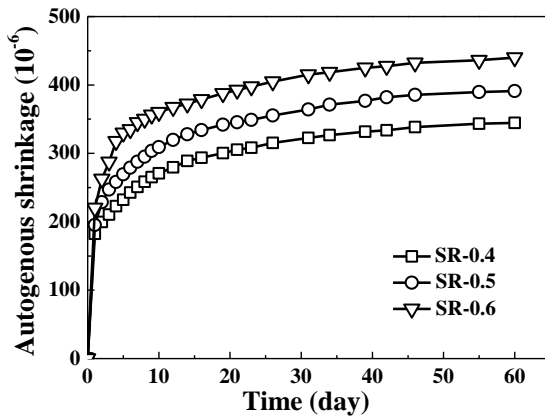


Figure 4. Effect of sand ratio

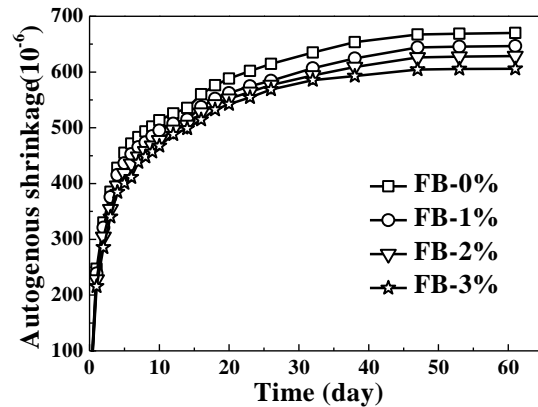


Figure 5. Effect of steel fiber volume

3.2 The mechanism research on UHPCC autogenous shrinkage

3.2.1 Comprehensive thermal analysis

Through a comprehensive thermal analysis test, the content of non-evaporated water was calculated to characterize the degree of cementitious material hydration. the content of non-evaporated water (W_n) can be calculated according to the following formula:

$$W_n = (m_1 - m_2) / m_2 \times (1 - L) - L$$

Where m_1 is the mass of the sample corresponding to the TG curve at 105°C ; m_2 is the mass of the sample corresponding to the TG curve at 1000°C ; L is the loss on ignition (expressed in mass fraction) of the cementitious material at 105°C , it can also be converted according to the cement and mineral admixture mass fraction in cementitious material and the loss of each component. The calculated content of non-evaporated water of different water-cement ratio slurries is shown in table 4.

Table 4. Non-evaporated water content in the slurry of different water-cement ratio

No.	The content of non-evaporated water (%)	
	7d	14d
W/B-0.16	10.7	12.0
W/B-0.20	12.2	13.7
W/B-0.24	15.1	15.6

As can be seen from the table, under all ages, the content of non-evaporated water decreases with the decrease of the water-cement ratio, indicating that the smaller the water-cement ratio, the smaller the degree of hydration of the slurry. This is because the water-cement ratio is reduced, the amount of water that can be supplied internally to hydrate the cementitious materials is reduced. In addition, since the water-cement ratio is decreased, the capillary porosity of hydration products is low and the pore diameter of the pores is small, making it is difficult for the water that supplying to cement and hydrating the cementitious materials to move to reaction area, resulting in the reaction rate reduced, thereby reducing the degree of hydration of cementitious material^[14].

3.2.2 Mercury Intrusion Method

The pore size distributions of three groups of cement-based composites with different ratios of water-binder and three mixed mineral admixtures are shown in figure 6 and figure 7, and the pore sizes are shown in figure 8. From figure 6 and figure 7, it can be seen that the most probable aperture of cement-based material decreases with the decrease of water-cement ratio. The most probable pore diameters are 0.24 μm , 12.25 nm and 17.11 nm and 21.10 nm respectively when the water-cement ratio are 0.16, 0.20 and 0.24 respectively, indicating that with the water-cement ratio decreases, the pore size is refined and the pore structure is improved. From Fig. 9, it is found that the porosity of cement-based composites decreases with the decrease of water-cement ratio. When the water-cement ratio decreases from 0.24 (18.13%) to 0.20 (13.35%) and 0.16 (10.08%), the 14d porosity decreased by 26.4% and 44.4% respectively. In addition, the porosity decreases with age, mainly due to the compact effect of the hydration product when it is hydrating.

During the autogenous shrinkage process, Self-desiccation mainly occurs in the capillaries, and the internal liquid surface of the capillary water drops and the curvature of the meniscus becomes larger, resulting in a larger surface tension. The pore radius distribution of liquid surface, that is, the pore size distribution in the cement-based composite slurry, allows the autogenous shrinkage to be studied in conjunction with the pore size distribution of the material. Related literature^[15] studies have shown that 5 ~ 50 nm pores are the main area which self-contraction occurred. Therefore, the decrease of the water-cement ratio will refine the pore structure and increase the number of pores with 5 ~ 50 nm pore size, leading to the increase of capillary pressure under the self-desiccation effect, thereby increasing the autogenous shrinkage of the cement-based composite.

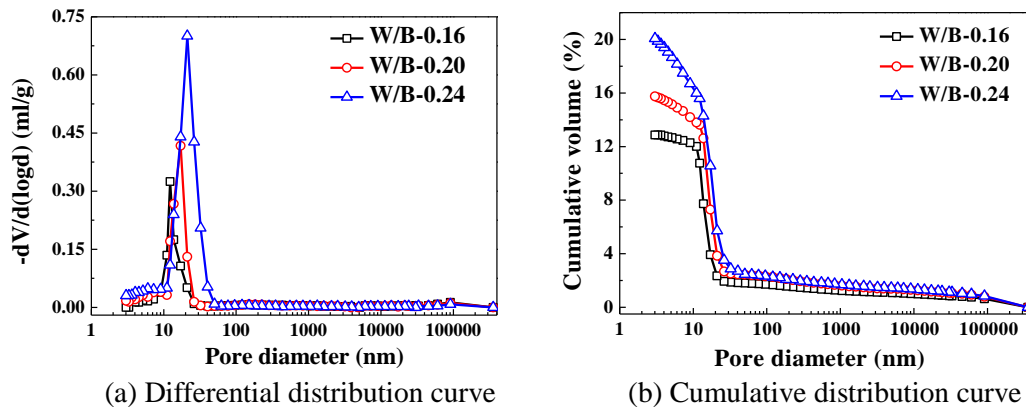


Figure 6. Pore size distribution of paste with different W/B in 7d

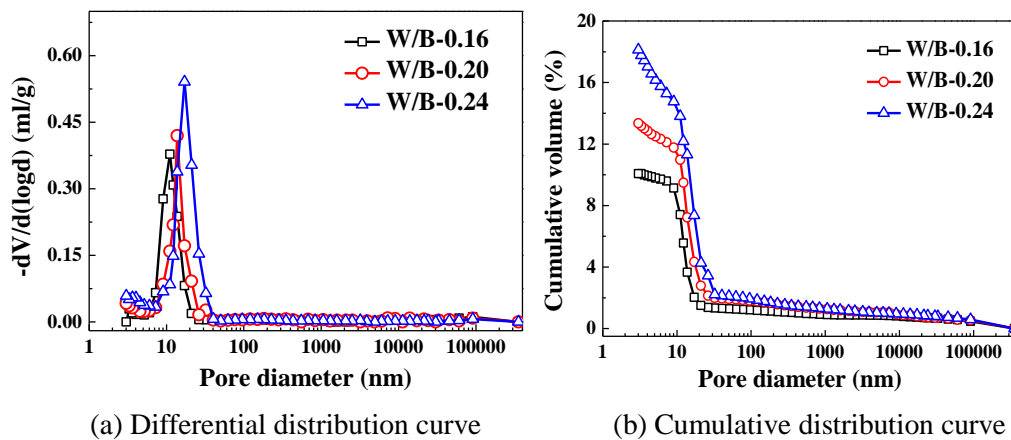


Figure 7. Pore size distribution of paste with different W/B in 14d

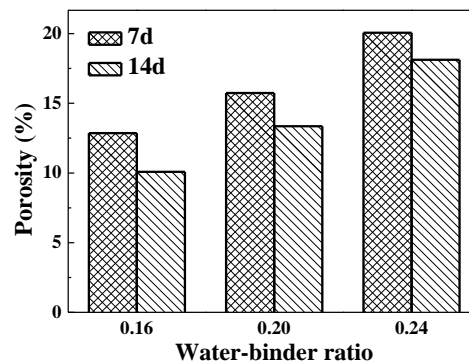


Figure 8. Effect of W/B on porosity of UHPCC

According to the test of non-evaporable water content and pore structure parameters, the water-binder ratio is decreased, the content of non-evaporated water is reduced, and the degree of hydration is reduced, which is a positive effect for autogenous shrinkage deformation. However, increasing the volume fraction of 5~50 nm pores increases the meniscus curvature, resulting in an increase in surface tension, which is manifested by an increase in the rate and extent of capillary negative pressure under seal conditions, an increase in self-dessication effect, which is a negative effect on autogenous shrinkage. The superposition of positive and negative effects shows that the autogenous shrinkage decreases with the increase of water-cement ratio, indicating that self-dessication effect plays a dominant role in the autogenous shrinkage factors.

4. Summary

- (1) The self-designed vertical dial gauge holder measures 1d autogenous shrinkage value, with the water-cement ratio decreased, the autogenous shrinkage increased significantly, the water-cement ratio decreased from 0.24 to 0.20, 0.16, 60d autogenous shrinkage value increased by 14.4% and 25.4% respectively.
- (2) Aggregate addition significantly inhibited the autogenous shrinkage of UHPCC. 60d autogenous shrinkage decreased with the decrease of the binder-aggregate ratio. When the aggregate volume fraction increased from 42.3% to 59.5% and 68.8%, the autogenous shrinkage value decreased by 29.7% and 38.1%. Volume stability has an extremely important role and significance.
- (3) The smaller proportion of coarse aggregate in aggregates, the greater autogenous shrinkage value, the greater sand rate, the greater autogenous shrinkage. When the sand ratio increases from 0.4 to 0.5, 0.6, the autogenous shrinkage value. Respectively, an increase of 13.3%, 15.9%. The inhibition effect on short fine steel fibers after 1d autogenous shrinkage is not obvious.
- (4) From DSC-TG and MIP microscopic analysis technology, decreasing of water-binder ratio, the content of non-evaporating water decreased, the degree of hydration decreased, which is a positive effect for shrinkage deformation; however, 5 ~ 50nm capillary volume fraction increases, the surface tension increases, the capillary negative pressure increases, the speed and extent are increased, that is to say the self-dessication effect increases, which is negative for the autogenous shrinkage effect. The superposition of positive and negative effects shows that the autogenous shrinkage decreases with the increase of water-cement ratio, indicating that self-dessication effect plays a dominant role in the autogenous shrinkage factors.

References

- [1] Igarashi S, Bentur A, Kovler K. Autogenous shrinkage and induced restraining stresses in high-strength concretes *J. Cement and Concrete Research*. 2000, 30(11):1701-07.
- [2] X.M. Kang. Study on dry shrinkage and autogenous shrinkage performance of high strength concrete *J. Journal of Southwest University of Science and Technology*. 2012(1):37-39.
- [3] L. Jin, Y. Yang. Experimental study on the autogenous shrinkage temperature dependence of high strength cement mortar *J. Journal of Lishui university*.2008(2):46-48.
- [4] Min K, Jung H, Yang J, et al. Shrinkage characteristics of high-strength concrete for large underground space structures *J. Tunnelling and Underground Space Technology*.2010,25(2): 108-113.
- [5] Z.H.He, C.X.Qian, G.F. Qian, et al. Influence of concrete components on internal relative humidity and autogenous shrinkage under equal strength *J. Function Material*.2011(2):222-225.
- [6] Q.B. Yang. Study on autogenous shrinkage mechanism of high performance concrete *J. Journal of the Chinese Ceramic Society*. 2000(S1):72-75.
- [7] H.S. Xu, Z.W. Jiang. Study on the change of relative humidity and autogenous shrinkage of high performance concrete *Journal of Chongqing Jianzhu University*.2004(2):121-125.
- [8] Jiang Z, Sun Z, Wang P. Autogenous relative humidity change and autogenous shrinkage of high-performance cement pastes *J. Cement and Concrete Research*. 2005, 35(8): 1539-45.
- [9] Yoo S W, Kwon S, Jung S H. Analysis technique for autogenous shrinkage in high performance concrete with mineral and chemical admixtures *J. Construction and Building Materials*. 2012, 34(0): 1-10.
- [10] C. Wang. Y.W. Wang, X.C. Pu. Autogenous shrinkage characteristics and mechanism of ultra-low water cement concrete *J. Journal of Building Materials*.2010(1):75-79.
- [11] H.B. Lin, C. Wang, Y.J. Zeng. Study on shrinkage deformation and cracking of steel fiber super high strength concrete *J. Concrete*.2011(5): 80-83.
- [12] Y.L. Guo, Y. Li, D. Huo. Study on effect of aggregate and fiber amount on early autogenous shrinkage of concrete *J. China Concrete and Cement Products*. 2006(3): 50-52.
- [13] H.J. Ba, W.M. Zhang. Effect of aggregate physical property on early autogenous shrinkage of commercial concrete *J. Ready Mixed Concrete*.2004(2): 10-14.
- [14] C. Wang. Study on the preparation, structure and properties of super high performance concrete *D.Chongqing University*, 2005.
- [15] Li Y, Bao J, Guo Y. The relationship between autogenous shrinkage and pore structure of cement paste with mineral admixtures *Construction and Building Materials*.2010, 24(10):1855-60.