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Water desorption characteristics of saturated lightweight fine aggregate in ultra-high performance concrete

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Abstract : In this study, the water desorption behavior of saturated lightweight fine aggregate (LWA) in ultra-high performance concrete (UHPC) was systemmically investigated using isothermal calorimetry, relative humidity (RH), mercury intrusion porosimetry, X-ray microtomography methods, etc.. The LWA with high porosity and coarse pore structure exhibited high absorption and easy desorption at high RH. The results indicate that a large amount of water in LWA was released before setting, resulting in an increase of water to binder ratio, which had an adverse effect on the performance. However, the water absorbed in LWA released fast after 6 h, inducing an internal curing effect. Mechanism on a "four-stage desorption" driven by capillary pressure and RH gradient was proposed. The water desorption that is beneficial for the internal curing is calculated. The results indicated that the internal curing efficiency could be enhanced by increasing LWA content and reducing its pore size.

Key words: Ultra-high performance concrete; Water desorption; internal curing; relative humidity; lightweight fine aggregate;

1. Introduction

UHPC refers to a new type of advanced cement-based material exhibiting great mechanical properties and durability, which represents the highest development of high performance concrete [1-3]. However, the typical UHPC exhibits very high autogenous shrinkage due to low water to binder ratio, high content of superfine materials, absence of coarse aggregate and high content of cementitious materials [4-6]. Many methods have been applied to reduce the autogenous shrinkage, including the addition of expansive agents, coarse aggregate and internal curing materials [7-9]. Among these methods, introduction of internal curing materials such as super absorbent polymer (SAP), LWA and rice husk ash (RHA) can reduce the autogenous shrinkage effectively[10-12]. As the hydration products in bulk form occupy less space than water [13], the hydration reactions are accompanied by chemical shrinkage. The chemical shrinkage will produce physical shrinkage before setting and produce a self-desiccation due to the formation of partially-filled pores [14, 15]. The pore solution menisci remaining in partially filled pores will create a measurable capillary pressure, resulting in autogenous shrinkage. In the mixtures with lower water to binder ratios, this capillary pressure is higher due to the formation of vapor filled cavities in smaller radius of curvature [16]. The water desorption of saturated internal curing materials can provide additional readily-available source of water so that the capillary pores of matrix remains saturated, thus reducing the autogenous stresses and strains [10, 15]. The water desorption is a competition of water between internal curing materials and matrix. The

water in larger scale pores can be released into smaller pores motivated by relative humidity [17]. When the water in internal curing material is exhausted, the capillary stress and autogenous shrinkage will rapidly increase over time. Then, the water desorption of internal curing materials will affect the development of autogenous shrinkage, hydration and performance of concrete [18].

According the previous studies [11, 19], LWA is more effective in the reduction of shrinkage than other internal curing materials, as the water desorption of LWA is driven by capillary action. Therefore, the effects of saturated LWA on the performance of UHPC have been investigated. Some studies showed that the LWA had an adverse effect on the mechanical properties of UHPC [19, 20], while the enhancements of durability and mechanical properties by adding appropriate amount of LWA were also reported [19, 21]. These differences are certainly depended on the water absorption and desorption properties of LWA. The LWA has a complex behavior of water desorption under capillary action and RH gradient during hydration. This complex process is closely related to its effect on the performance of concrete. However, there is limited information on the water desorption of LWA in UHPC, and most of existing literature focus on that in the high performance concrete and ordinary concrete. The capillary pore structure and RH evolution of UHPC are rather different from those of ordinary concrete due to the large amount of superfine particles and low water to binder ratio [22, 23]. This will influence the process of water desorption of LWA and make it difficult to control the autogenous shrinkage. As a result, the water desorption process

of LWA in UHPC become a subject of great significance.

LWA is an artificial porous material, which is first produced in the 1930's for the production of lightweight blocks. It has been used in many applications such as masonry blocks, horticultural blends, filtration and civil engineering [24]. Also, The LWA has been used as an internal curing materials in high performance concrete due to its porous structure characteristic [25-28]. The results indicated that water desorption of LWA had significant effects on the internal curing effect, mechanical strength and pore structure evolution of concrete [27, 29, 30]. The primary hydration heat was moved up by adding LWA [10, 19]. In addition, the development of cumulative heat of hydration and degree of hydration were closely related to the water desorption of LWA. Several studies have investigated the desorption properties of LWA in concrete. For example, Landgren et al. investigated the absorption and desorption properties of coarse LWA used in US [31]. Bentz et al. determined the desorption isotherms by using salt solution to evaluate the water that was released into concrete due to self-desiccation [32], and found that most of the water within LWA was observed to be released during the first day's hydration [33]. Meanwhile, the water desorption from LWA exhibited a one-to-one agreement with measured chemical shrinkage. The time and distance of water movement from saturated LWA to cement paste were investigated by X-ray technique, which was important for mix design, shrinkage and stress development of concrete [34]. It should be noted that an internal curing affect zone around LWA was formed, as more water was consumed by this zone after setting [35]. Trtik et al. tested

water desorption of LWA using neutron radiography between 0.5 h and 20 h. It was found that the water desorption was a fast process, and the water was distributed homogeneously from the LWA to at least 3 mm into the paste [36]. In general, these literatures indicate that the water desorption process is of great significance for the working mechanism of LWA on the microstructure and performance of concrete.

The UHPC is different from normal concrete and high performance concrete, mainly reflects in its very low water to binder ratio and large amount of superfine particles, leading to a dense surrounding for LWA. This surrounding will influence the water desorption process of LWA, which leads to a different internal curing effect in UHPC compared to that of normal concrete. The previous studies showed that the LWA had an adverse effect on the performance of UHPC [19, 20], especially for UHPC with large amount of LWA. Generally, investigations on the effect of LWA on the performance of UHPC and the internal curing efficiency in UHPC are still very few, and the water desorption behavior of LWA in UHPC is also not clear.

The objective of this study is to investigate the water desorption characteristics of saturated LWA in UHPC and quantify the amount of water that releases during different curing ages. The water desorption behavior of LWA in UHPC was preliminarily characterized through measuring the internal RH development, hydration characteristics, workability and free water evolution. To obtain a deep understanding of the water desorption mechanism of saturated LWA in UHPC, the chemical shrinkage, autogenous shrinkage, X-ray microtomography images, pore structure and water

desorption of LWA under RH evolution of UHPC were measured. The water desorption process of LWA in UHPC was revealed on the basis of these measurements, and the amount of released water at different ages as well as the utilization rate of the internal curing water were quantified.

2. Experiment

2.1 Materials

Portland cement, silica fume and fly ash were used as cementitious materials. Their chemical compositions were listed in Table 1. LWA and quartz sand with the size between 0.15 mm and 1.18 mm were used as aggregates. The LWA was produced by expanded shale. The chemical composition of LWA was also listed in Table 1. The specific density of quartz sand is 2530kg/m^3, and the wet specific density of LWA is 1510kg/m^3. The water absorption of LWA is 10.1%, which was tested after soaking in water for 24 h. Steel fiber (length=13mm, diameter=0.22mm) and superplasticizer were used as received. The dosage of steel fiber was 2% of the total volume of UHPC. The superplasticer (produced by Sobute New Materials CO.,LTD) and tap water were also used.

Table 1 Chemical compositions of cementitious materials (wt. %)

Oxide	SiO_2	Al_2O_3	CaO	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	LOI
Cement	21.29	4.18	62.28	3.34	2.64	2.40	0.13	0.59	2.09
Silica fume	88.29	0.14	0.92	0.19	1.51	3.21	0.14	0.17	5.26
Fly ash	54.69	12.71	17.48	4.61	0.97	1.68	1.75	3.18	1.79
LWA	65.46	16.75	1.08	7.63	0.45	2.43	3.82	0.94	0.27

2.2 Specimens preparation

Table 2 Mix proportion of the UHPC (kg/m^3)

Num.	Cement	Silica fume	Quartz sand	Fly ash	LWA	Superplasticizer	w/b
C0	720	160	1250	80	0	9.60	0.180
C0-1	720	160	1250	80	0	9.60	0.185
C0-2	720	160	1250	80	0	9.60	0.190
C0-3	720	160	1250	80	0	9.60	0.195
C0-4	720	160	1250	80	0	9.60	0.200
C0-5	720	160	1250	80	0	9.60	0.205
C0-6	720	160	1250	80	0	9.60	0.210
C0-7	720	160	1250	80	0	9.60	0.203
C1	720	160	1000	80	150	9.60	0.196
C2	720	160	750	80	300	9.60	0.211
C3	720	160	500	80	450	9.60	0.227
C4	720	160	250	80	600	9.60	0.243

The mixture proportion of UHPC is shown in Table 2. The LWA was used to replace quartz sand. Before use, it was presoaked in water for 24 h. The mix process was adjusted when LWA was added. Firstly, the cementitious materials should be mixed with water and saturated LWA for 3 min. Then, the quartz sand was added and mixed for another 3 min. The contents of LWA were calculated based on the volume replacements of quartz sand. In this study, the UHPC mixtures with w/b ratios of 0.180, 0.185, 0190, 0.195, 0.20, 0.205 and 0.210, were prepared for slump flow test. Also, the UHPCs with an initial w/b ratio of 0.180 and different amounts of LWA were prepared to investigate the water desorption process of LWA. As different amounts of LWA were incorporated into the mixtures, the real w/b in Table 2 referred to the mass ratio of total water (including the additional water brought by saturated LWA) to binders. The cast UHPC specimens containing different amounts of LWA were sealed with plastic films

to prevent moisture exchange and cured at the temperature of 20℃. These specimens were measured with relative humidity, pore structure and mechanical properties.

2.3 Methods

(1) Hydration characteristics

The heat flow and cumulative heat of samples with and without LWA were monitored by using an isothermal calorimetry (model TAM Air, Thermometric). The test temperature was 20ºC±0.1ºC. The samples were tested at 2 h after mixing with water. Each sample contained about 5 g of dry binders. The testing time lasted for 72 h.

The non-evaporable water content of samples without LWA and with 450kg/m^3 of LWA at 1d, 3d, 7d, 14d and 28d of curing were measured. The method was usually used to evaluate the degree of hydration of cementitious materials[10]. The samples from the middle of UHPC were grounded and dried in an oven at 105℃ until the measuring mass was constant. Then, the powdered samples were heated at 1050℃ for 3 hours. Usually, the mass loss difference between105℃ and 1050℃ is considered as non-evaporable water. Meanwhile, the loss on ignition of binders was considered. Three replicates of each group were used to calculate the average value.

(2) Free water content

The free water contents of UHPC at different ages were measured by freeze drying under vacuum. The UHPC samples with 450 kg/m^3 of LWA and without LWA were prepared and cured at 20ºC±0.1ºC under sealing condition. Each sample was placed into freeze dry condition at 30 min, 6 h, 12 h, 18 h, 24 h, 3 d, 7 d, 14 d and 28 d. When

the mass of sample was constant, the mass loss due to freeze drying was considered as free water content.

(3) Internal relative humidity

Specimens with size of 100 mm×100 mm×100 mm were prepared for internal relative humidity test. A hole was reserved in each specimen by placing a palstic sleeve at a depth of 50 mm, and the wall of sleeve was removed and packaged by polyester net fabric. A sensor was put ino the hole to monitoring the RH and temperature. The accuracies of the measurement of RH and temperature are ±0.1% and 0.1℃. The measurement started at 15 min after mixing with water. The illustration of this measurement was shown in Figure 1.

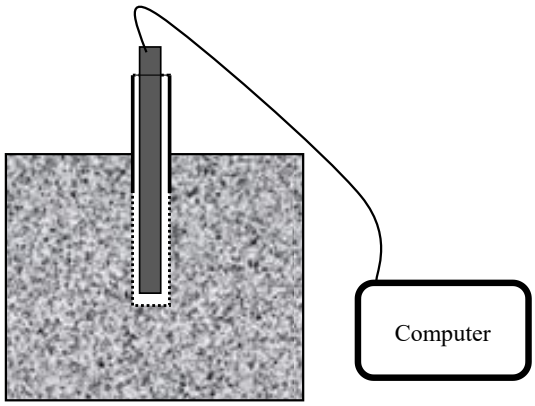


Figure 1 The illuration of relative humidity measurement

(4) Autogenous shrinkage and chemical shrinkage

The autogenous shrinkage was measured by a non-contact shrinkage deformation tester (model CABR-NES) according to the Chinese standard [37]. The specimens were covered with polyethylene film during testing. The autogenous shrinkage measurement was carried out after setting, the testing interval was 1 min. The chemical shrinkage

was tested according to the dilatometry in ASTMC 1068 [38]. The drop in the level of water in a hydrating UHPC was measured by a pipette, the volume change of water was regarded as the chemical shrinkage of UHPC. The measurement was started at 1 h after mixing with water

(5) Pore structure

The pore structure of the UHPC with and without LWA were determined using nitrogen adsorption method. The specimens with the curing age of 12 h, 24 h, 3 d, 7 d and 28 d were tested. Before testing, the specimens were dried at 60°C. The mercury intrusion porosimetry (MIP) and nitrogen adsorption method were used to test the pore structure of LWA. The AutoPore IV 9500 series pore size analyzer (Micromeritics Instrument Corporation) was used for MIP method. The minimum and maximum pressures were 0.3 MPa and 414 MPa, respectively. A BELSORP-mini II made by Dutch Ankersmid company was used to measure the nitrogen adsorption and desorption isotherms.

(6) Workability

The slump flow of UHPC with 450 kg/m^3 of LWA and without LWA was tested according to Chinese test method for fluidity of cement mortar (GB/T2419-2005) [39]. In order to determine the water desorption before setting, the slump flow was tested at 5 min, 30 min, 60 min, 90 min, 120 min and 180 min. The slump flow of samples with different initial water to binder ratios of 0.185, 0.19, 0.195, 0.20 and 0.21 were tested at 30 min and 180 min. The slump flow of UHPC containing 150 kg/m^3, 300 kg/m^3 and 600 kg/m^3 of LWA was also tested at 30 min and 180 min.

(7) LWA water absorption

The water sorption of LWA was assessed by wild-mouth bottle and pipette. This method was similar to a previous method by using volumetric flask [35]. Figure 2 shows the diagrammatic sketch of this setup. The LWA was firstly dried at 105°C, and 100g LWA was placed in a wild-mouth bottle (250ml). The water was filled to achieve nearly 100% of capacity of the wild-mouth bottle and pipette, then it was vibrated for about 3 min to eliminate air bubbles among LWA particles. Finally, the scale of water level was recorded at 5 min, 30 min, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 7 h, 8 h, 9 h, 10 h, 11 h, 12 h, 13 h ….24 h. The absorbed water can be obtained by calculating the water recorded at different time. After that, the water absorption of LWA with a function of time can be obtained.

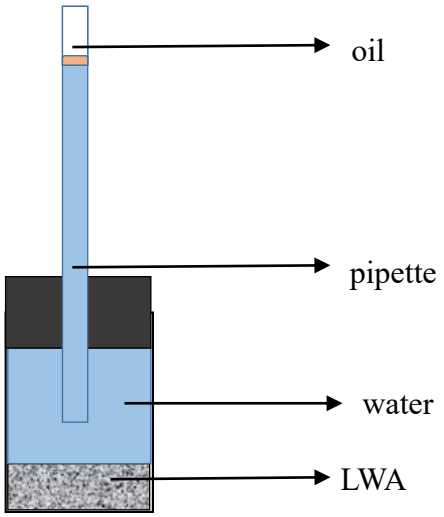


Figure 2 The diagrammatic sketch of setup to measure water absorption of LWA

(8) Water desorption capability

The water desorption of LWA can be described by the mass loss with a function of RH. A thermal-humidity test chamber was used to control the RH evolution. Before testing, the LWA was firstly dried at 105°C for 24 h and placed in tap water for 24 h

prior to testing. Then the LWA was patted to saturated-surface-dry and placed into thermal-humidity test chamber (RH 100% and temperature 20ºC±0.1℃) until the LWA achieved a constant mass. After the mass loss of sample was constant, the RH was changed in 1% steps to 90% [35, 40]. The mass loss was recorded, then the samples were dried at 105℃ to obtain the total water absorption.

The free water evaluation of LWA under the RH development of UHPC with and without LWA was also tested. The saturated-surface-dry LWA was placed in to a thermal-humidity test chamber. The temperature of the chamber was kept at 20±0.1℃. The RH evolution curves were set up according to the internal RH development of UHPC with 450kg/m^3 of LWA and without LWA. The mass loss of LWA at different curing ages was measured.

(9) X-ray microtomography (CT)

An X-ray micro-CT scanner produced by Bruker CO., Ltd was used. The number of pixels in each section was 1024×1024 corresponding to 4 μm×4 μm for each pixel. The specimens were prepared with a polypropylen pipe with a diameter of 2 mm. After mixing, the UHPC mixture with LWA was cast into the pipes. The pipes were sealed until the testing date and placed on the table of micro-CT machine. It should be noted that the LWA used in this study was saturated by CaI solution (the solubility is 150g/100g water). The same position of the sample was scanned at 6 h, 12 h, 24 h and 168 h. There were 1500 projection directions used in different scans. The average projection data was used for image reconstruction algorithm based on a filtered back-projection method [41].

(10) Mechanical properties

The UHPC specimens containing different amounts of LWA were casted for

compressive strength measurement. The size of specimens was 40 mm×40 mm×160 mm. The specimens were demolded at 1 d and cured at 20±0.1℃ under sealing condition. The compressive strength was tested with a loading rate of 2.4 kN/s at the age of 3d, 7d and 28d. Three specimens were performed to calculated the average value.

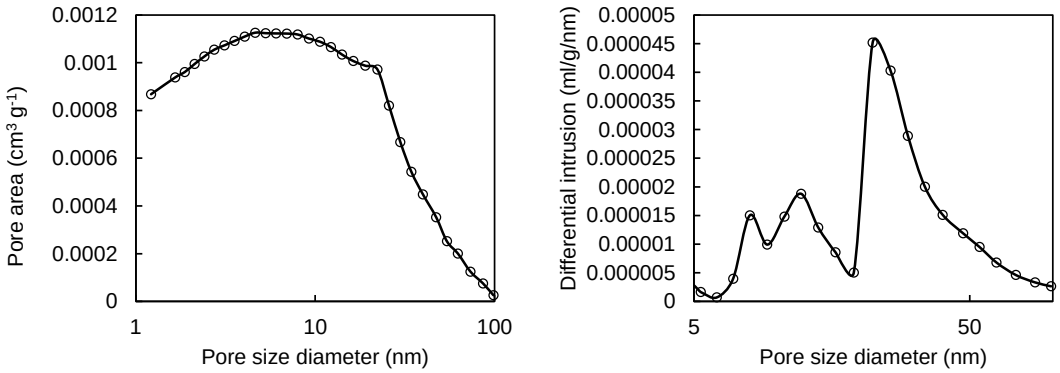
3. Results and discussion

3.1 LWA characterization

3.1.1 The pore structure of LWA

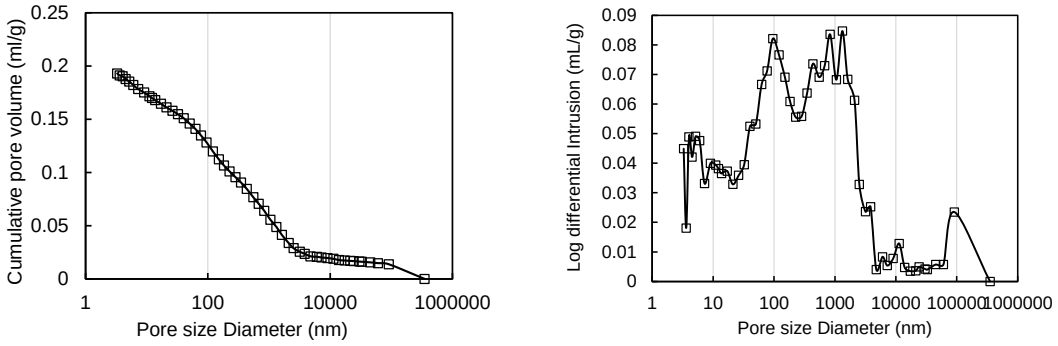
The pore structure of LWA was measured by nitrogen adsorption and MIP methods. The test results are shown in Figures 3 and 4 respectively. From the MIP results, the cumulative pore volume is 0.193ml/g. The pore size distribution shows that there are two peaks between 10 nm and 5000 nm, and a large number of pores with a size less than 100 nm can also be observed. However, the nitrogen adsorption test results show that the number of connective pores below 100 nm is low. As the nitrogen adsorption is nondestructive method, it can represent the fine pore structure accurately. Therefore, the pore structure obtained from MIP method seems to be incorrect, especially for the fine pores. Meanwhile, the porosity from MIP method is much higher than the actual porosity. It is likely that some non-connective pores in LWA are destroyed by pressure, and the pore structure is collapsed during testing. In addition, some macropores in LWA are presented as nano-pores in MIP test results, which is also related to the effect of ink-bottle pore [42]. Therefore, the MIP method may not be used to indicate the pore structure of LWA accurately. Considering the pore structure tested by these two methods,

it can be concluded that the size of the main pores in LWA are larger than 100 nm, which is much larger than the main capillary pores in UHPC. Previous studies have indicated that the water will move from coarser pores to finer pores during drying [35, 43]. So the water in LWA will preferentially move from the LWA to the cement paste. This pore structure characteristic of the LWA indicates that the water in these coarse pores will be released into matrix easily during hydration. In order to evaluate the water desorption ability of LWA in UHPC, the water absorption and water desorption capability of LWA should be measured.



(a) The cumulative pore volume (b) The differential intrusion

Figure 3 The nitrogen adsorption test results of LWA



(a) Cumulative pore volume (b) Log differential intrusion

Figure 4 The MIP test results of LWA

3.1.2 Water absorption of LWA

The water absorption capability of LWA in UHPC is closely related to the effect of LWA on the mechanical properties, workability, hydration, autogenous shrinkage and durability [29, 44, 45]. Excessive and insufficient water absorption may lead to poor internal curing effect on the performance of concrete, for example, the reduction of mechanical properties and durability [35]. The water absorption process of LWA was tested by the device shown in Figure 2. The water absorption capabilities of LWA of different particle sizes are present in Figure 5. The water absorption of LWA is obviously influenced by the particle size. In fact, the water absorption increases with the increasing size of LWA. Larger LWA have larger porosity, and the voids become coincide with the fracture surface. The low capability of water absorption can be observed while the porosity decreases. The water absorption is rapid during the first 3 h, which is due to absorption force from emptying pores in LWA. The water absorption still proceeds with a decreasing rate between 3 h and 24 h. The water absorption rate of LWA with size of 0.15-1.18mm is 10.1% at 24 h. After that, the water may still get into the LWA, and the LWA becomes over-saturated. But the water absorption rate at 24 h is used for mixture design [46]. In general, the LWA used in this study possesses a relatively high water absorption capability and shows potentials to be an ideal internal curing material. The amount of additional water and amount of LWA required for internal curing is closely related to its absorption capability. Thus, the proportion of LWA used in this study and the actual water to binder ratio is calculated based on the

water absorption capability.

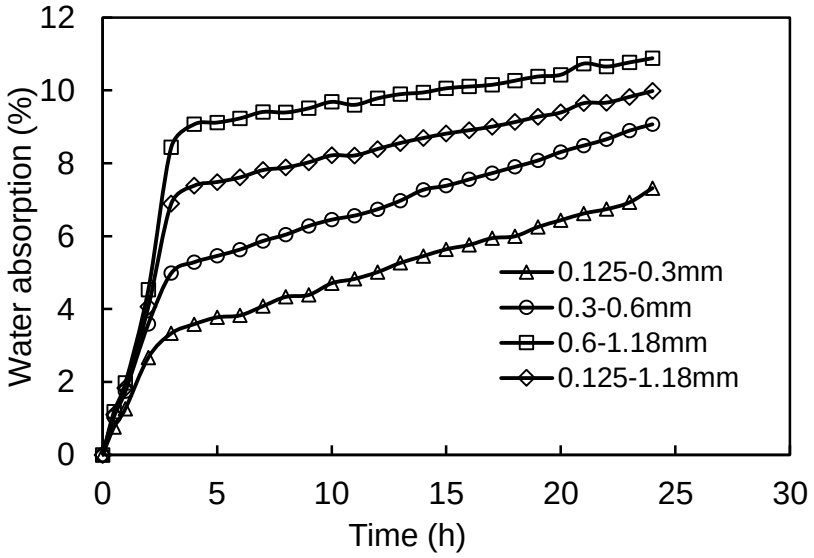


Figure 5 The water absorption process of LWA

3.1.3 Water desorption of LWA

Figure 6 shows the development of mass loss of saturated LWA vs. time. It can be seen from Figure 6 that the water content decreases rapidly with the decreasing RH. The change of mass decreases when the LWA approaches to equilibrium. Then, the mass loss at each RH decreases with the decreasing RH. This would be consistent with the volume and size of pores that water is lost. It should be noted that the majority of water has been released at very high RH. It can be seen from Figure 6 that more than half of entrained water has already been released at 99% RH, and about 94% of total entrained water in LWA has been desorbed at 98% RH. This indicates that most of the absorbed water releases at relatively high RH. Usually, the water in LWA should be released at relatively high RH to participate in the hydration of cement [47]. Therefore, the LWA used in this paper is an efficient internal curing material, which can promote

the hydration of cement at the early age. The entrained water in LWA will release rapidly and show internal curing effect on the UHPC.

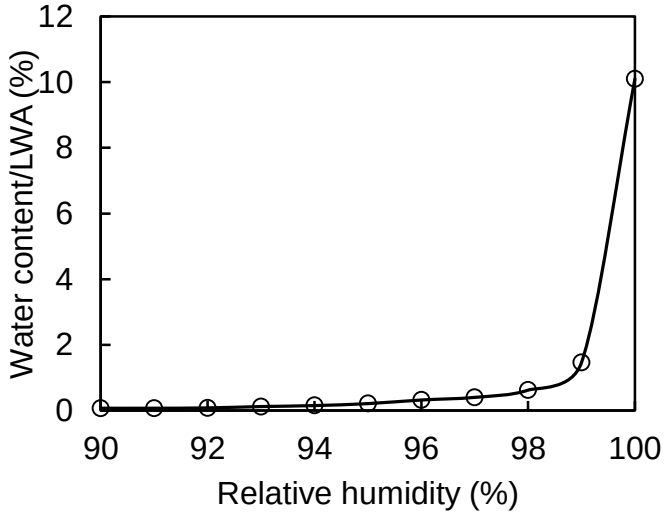


Figure 6 The water desorption behavior of the LWA

3.2 Effect of LWA on the hydration, microstructure and mechanical properties evolution of UHPC

3.2.1 Internal relative humidity and hydration characteristics

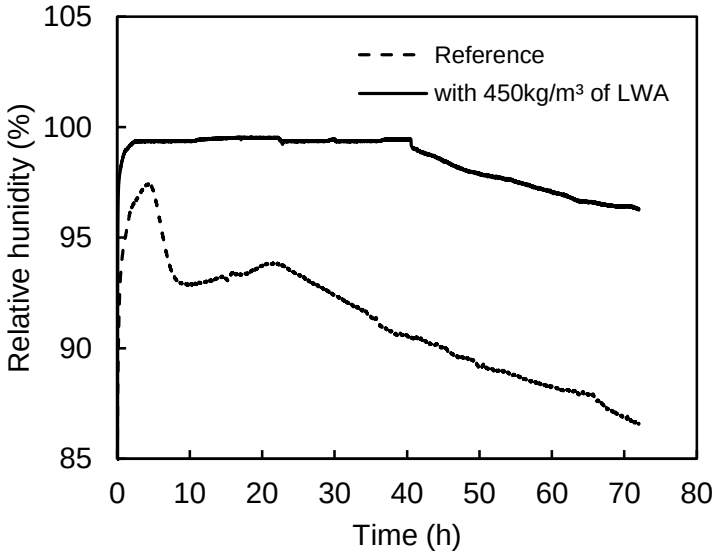


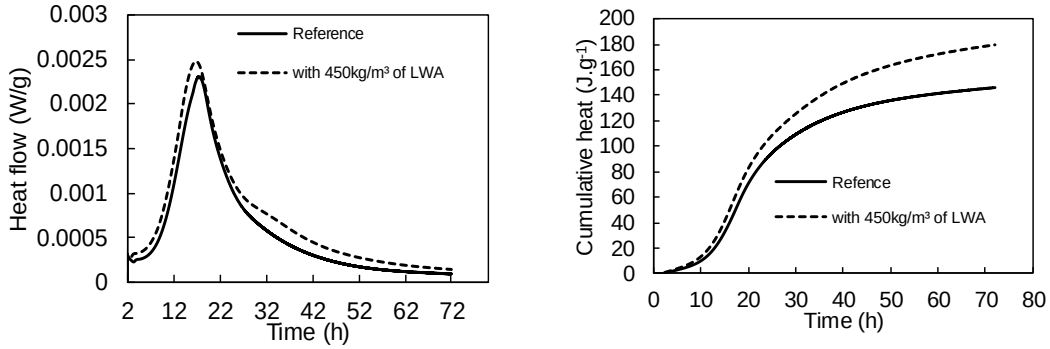
Figure 7 Internal relative humidity of UHPC with and without LWA

Figure 7 shows the internal RH vs. curing time of UHPC without LWA and with

450kg/m^3 of LWA. It can be observed that the RH is obviously improved, and the reduction of RH is delayed [21]. In addition, the UHPC with LWA exceeds a high RH of 99.3% at about 3 h and keeps the RH high. The increase of RH and non-reduction of humidity at early age is related to the water desorption of LWA. Actually, it is the entrained water from LWA makes the capillary pores saturated and improves the internal RH at the early age. It should be noted that much water has released before setting (before 6 h), which improves the RH at early age. This water is not for internal curing but increases the initial water to binder ratio of UHPC, which is expected to be adverse to the performance of UHPC.

The internal RH is rather low in reference UHPC due to the low water to binder ratio, as a result, a high self-desiccation is present. The maximum internal RH of reference sample is 97.4% at about 3 h. This means that some pores are empty even when the UHPC is still mixture. However, the water desorption of LWA improves the internal RH at early age, and the internal RH of UHPC mixture with LWA reaches to about 99.3% at 3 h, implying that the empty pores are nearly saturated. This further leads to the delay of occurrence of self-desiccation. Therefore, a low autogenous shrinkage will be found [19, 21]. From the development of internal RH, it can be conclued that the addtion of LWA improves the internal RH of UHPC not only at early age but also that at later age. The improvement of RH owing to water desorption can truly reduce the autogenous shrinkage and risk of cracking. However, some water is released before setting when the UHPC is still mixture, which is unexpected and makes

negative influence on the performance.



(a) Heat flow (b) Cumulative heat

Figure 8 Hydration heat release rate and cumulative heat of UHPC

Since the internal RH was changed by adding LWA, the hydration was sure to show some differences. Figure 8 shows the isothermal calorimetry heat curves of UHPC with 450kg/m^3 of LWA and without LWA. The hydration heat is obviously influenced by the water desorption of LWA. As the internal RH of UHPC mixture is increased after adding saturated LWA (shown in Figure 7), the heat flow before setting (before 6 h) is a little higher than that of reference sample. This also confirms that some water is released before setting, which increases the water to binder ratio of UHPC. For the age between 6 h and 24 h, the heat flow is also increased by adding LWA. The water desorption of LWA accelerates the hydration of cementitious materials during the first day [33, 48], but the cumulative heat shows little difference at the first 24 h. Moreover, there is a shoulder at the age between 24 h and 72 h (show in Figure 8(a)), showing a higher heat flow compared to reference sample. The improvement of heat flow and cumulative heat is closely related to the water released from LWA. This indicates that much water is released at the age between 24 h and 72 h. From the isothermal calorimetry heat results, it can be seen that water desorption in LWA plays an important

role in controlling the hydration of UHPC. The water released from LWA improves the internal RH and further influences the hydration process. It should be noted that the internal curing effect become significant after the first day, owing to the rapid decrease of internal RH of reference sample. From the hydration heat evolution, the hydration is closely related to water desorption behavior of LWA, the water released from LWA not only improves the hydration during the first day but also promotes the hydration in the following stage, indicating a continuous water desorption process of LWA. The increase of hydration heat implies the improvement of hydration degree, which may bring the enhancement of pore structure.

In addition, in order to evaluate the influence of LWA on the degree of hydration, the non-evaporable water content of samples without LWA and with 450kg/m^3 of LWA at 1d, 3d, 7d, 14d and 28d of curing were measured. The test results show that the water desorption increases the degree of hydration at early and later stages of curing. As the additional water to binder ratio of C3 is 0.047, which is incorporated in the saturated LWA. The improvement of non-evaporable water content will be 26.1%, when all the additional water from LWA becomes chemical water. However, the actual improvement of non-evaporable water content at 28d is 13.4%, which is much lower than that the expected improvement of non-evaporable water content. The non-evaporable water content is commonly used to evaluate the degree of hydration of cementitious materials, and the increase of non-evaporable water content is equal to the development of degree of hydration. Generally, the degree of hydration is obviously increased by adding LWA.

The improvement of degree of hydration may change the pore structure of matrix and further influence the mechanical properties.

Table 3 The non-evaporable water content

Time (d)		1	3	7	14	28
Non-evaporable water content (g/g binder)	reference	0.118	0.121	0.135	0.139	0.144
	With 450kg/m^3 of LWA	0.123	0.128	0.153	0.157	0.163
Improvement (%)	With 450kg/m^3 of LWA	4.95	5.83	13.05	13.29	13.39

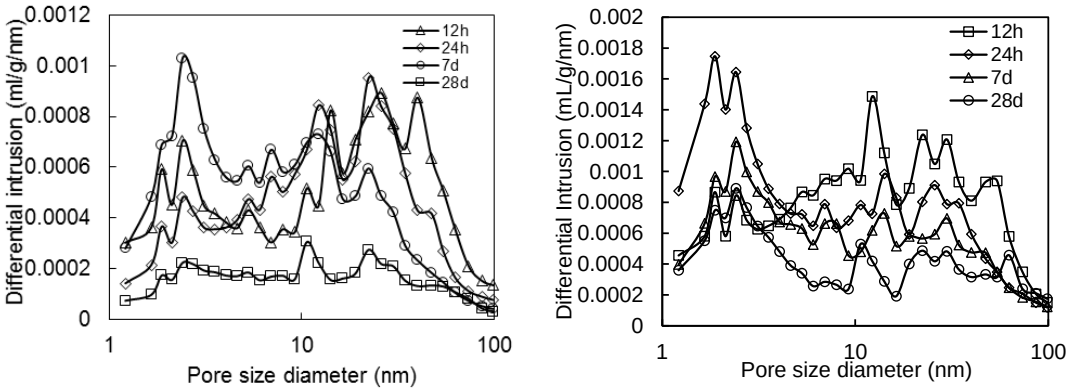
3.2.2 Evolution of pore structure

The pore structure of UHPC (without and with 450kg/m^3 of LWA) were tested by nitrogen adsorption method. As the main pores in LWA are larger than 100 nm, the influence of porous LWA on the test results can be neglected. The test results can represent the pore structure of the matrix. Figure 9 shows the pore size distribution of UHPC at different stages of curing. It can be observed that the development of pore structure of UHPC with and without LWA (Figure 9) both show decreasing trends, but there are still some differences in pore size distribution and variation process. As is shown in Figure 10, the porosities of both samples decrease rapidly with the increasing curing age, but the reduction of porosity of UHPC containing LWA is more significant than that of reference sample. It should be noted that the reduction rate increases with the increasing stages of curing. In addition, the porosity of UHPC with LWA is 0.0638cm^3/g at 12 h, indicating a higher porosity than that of reference sample. Generally, the water to cement ratio is one of the important factors influencing pore

structure, and the porosity will be increased and pores can be coarsen by improving the water to cement ratio [49]. Because the internal RH in UHPC mixture is very low (shown in Figure 6), the water in LWA is released after mixing due to RH gradient. The initial water to binder ratio thereby is increased. Therefore, it can be concluded that some water stored in LWA may be released when the UHPC is still with the state of mixture, leading to an increasing water to binder ratio. But the internal curing of LWA offsets this disadvantage in the following ages, as a result, the porosity of UHPC containing LWA is lower than that of reference sample at 24 h. Also, the reduction rate becomes more and more obvious as the curing age increases. Besides, the pore size distribution and its development of UHPC is significantly changed. The volume of coarse pores (>50 nm) is reduced by internal curing of LWA, but the amount of pores with the size below 50 nm shows an opposite trend. This indicates that the internal curing of LWA not only reduces the coarse pores but also increases the fine pores at different ages. Therefore, the average pore size is reduced due to internal curing. It is worth noting that the differences in proportion of fine pores (<50 nm) become more and more obvious with the increasing curing age, which means that the proportion of fine pores increases continuously compared to that of reference sample.

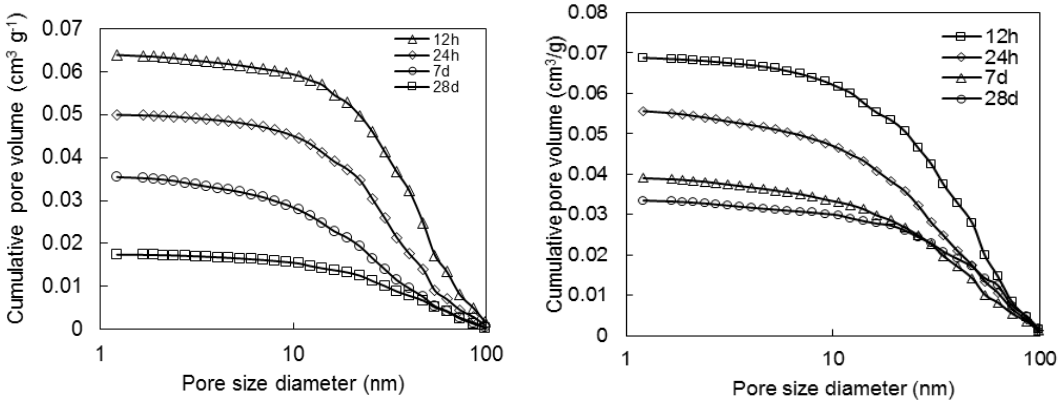
Based on the above analysis, the water desorption of LWA is closely related to the development of pore structure. The water desorption before setting shows an adverse effect on the porosity as well as the distribution of pore structure. But as the water desorption proceeds, this effect is overwhelmed by the beneficial effect of internal

curing. In general, the evolution of pore structure is closely related to the water desorption behavior of LWA in UHPC.



(a) with 450kg/m^3 of LWA (b) without LWA

Figure 9 The pore structure distribution of UHPC with and without LWA



(a) with 450kg/m^3 of LWA (b) without LWA

Figure 10 The cumulative pore volume of UHPC with and without LWA

3.2.3 Evolution of mechanical properties

The development of compressive strength of UHPC with 450kg/m^3 of LWA and without LWA is shown in Figure 11. The test results indicate that the compressive strength of UHPC containing LWA is lower than that of reference sample at early age (3 d), but it exhibits a higher compressive strength than that of reference sample at the

age of 7 d and 28 d. Compared with the reference sample, the compressive strength increases by 6.0% at 28 d when the 450kg/m^3 of LWA is presented. It should be noted that the 3d-compressive strength is reduced by adding LWA, which is due to the water desorption of LWA before setting and the high porosity of LWA. Although the matrix of UHPC containing LWA possesses a lower porosity than that of reference sample at 24h, the total porosity is obviously increased by porous LWA, leading to the reduction of mechanical properties. As the internal curing is on-going in the later time, the enhancement of matrix from internal curing overwhelms the initial disadvantages of the water desorption before setting. Therefore, the compressive strength of UHPC containing LWA is higher than that of reference samples at 7 d and 28 d.

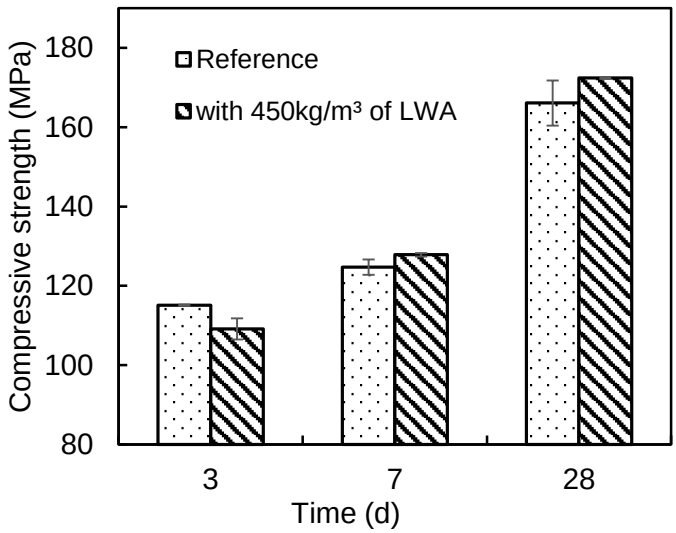


Figure 11 The compressive strength of UHPC containing different LWFA

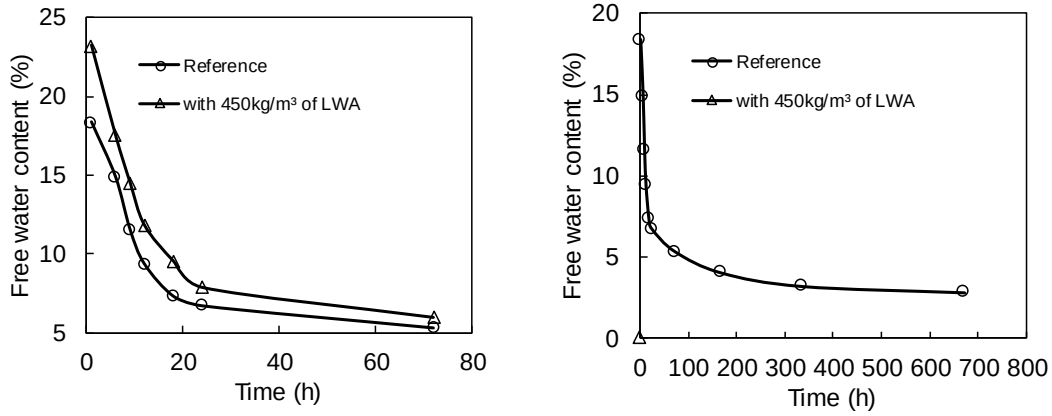
3.3 Water desorption process of LWA in UHPC

3.3.1 Free water evaluation

The free water evolutions of UHPC with and without LWA were measured to indicate the water desorption process of LWA in UHPC. The development of free water content of UHPC is shown in Figure 12. The experimental results show that the free water in UHPC with and without LWA is consumed rapidly during the first 24 h. But the difference in water content between UHPC with 450kg/m^3 of LWA and without LWA diminishes with increasing stage of curing. It is worth noting that the amount of the free water becomes similar at 14 d. This indicates that the free water stored in LWA is almost exhausted at 14 d.

During the first 24 h, there is about 15.34% free water that has been consumed in UHPC with LWA, which is much higher than that of reference sample (11.64%). The left free water content is 7.90% and 6.74% at 24h, which is corresponding to UHPC with and without LWA, respectively. This indicates that much moisture stored in LWA has released and participates in the hydration of cement paste during the first 24 h. From the pore structure shown in Figure 9 and Figure 10, these two samples possess similar porosity at about 12 h. But the water desorption of LWA promotes the hydration and reduces the porosity in the following curing age. Compared to the reference sample, the water released from LWA is at least 3.70% during the first 24 h, 0.50% between 24 h and 3 d, 0.63% between 3 d and 14 d and 0.12% between 14 d and 28 d, respectively. Much water releases into pores of UHPC, but it is difficult to distinguish from the total

free water. Therefore, it can be obtained from the evolution of free water, at least 76.00% of total water presoaked in LWA has been released at 24 h. Also, there is much water that participates in the hydration between 24 h and 14 d. After that, the water in LWA is almost exhausted, and the free water content in UHPC with and without LWA becomes similar. Therefore, it can be observed from the test results that most of water in LWA has been released at the early age, and this water fills into the empty pores and promotes the hydration of UHPC and reduce the autogenous shrinkage.



(a) 72h (a) 28d

Figure 12 Free water content evolutions of UHPC with and without LWA

3.3.2 Water desorption of LWA under the RH evolution of UHPC

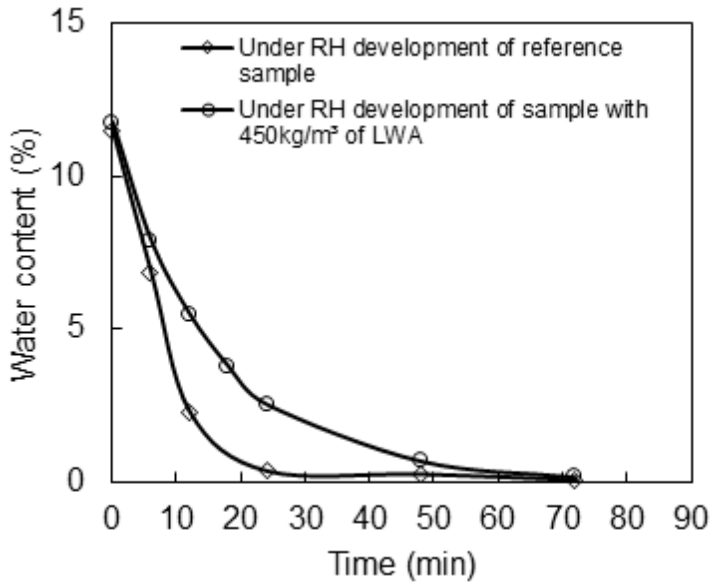


Figure 13 The water desorption of LWA under RH evolution of UHPC

The water desorption curves of wet LWA under RH development of samples with and without LWA are plotted in Figure 13. The test results show that the water releases rapidly during the first 20 h. Because the maximum value of internal RH curve of reference sample is only 97.4%, decreases quickly after 6 h and approximately 80.0% of total water has been released during first 12 h. Then, the water desorption slows down in the following time, and more than 95.0% of water has released at 24 h. After that, the water releases slowly in the following time. However, the water release is significantly reduced when the RH is improved (under RH development of sample with 450kg of LWA). Therefore, the differences in water desorption of these two curves are mainly depended on internal RH development. Compared to the water release in ordinary concrete [26], the low RH accelerates the desorption of water in LWA.

For the UHPC without LWA, it is possible that the water saturated in LWA releases rapidly when it is still mixture. This is mainly driven by the RH gradient. This water desorption before setting is adverse to the microstructure and mechanical properties due to increasing water to binder ratio. Moreover, the internal RH is significantly increased by adding saturated LWA, so the motivation from RH gradient is expected to be weakened. Actually, the water desorption of LWA in UHPC depends on not only on the RH gradient but also the pressure of capillary pores [36]. The actual water desorption can be accelerated by capillary pressure, but the decreasing RH gradient (relatively high internal RH) will reduce the influence of capillary pressure. Therefore, the water desorption of LWA in UHPC will be rapid in the first 3 h, but the water desorption would be slow down due to the relatively high RH. This water desorption in UHPC is expected to be more rapid than the measured water desorption of LWA under the RH evolution of UHPC, owing to the presence of capillary pressure.

3.3.3 Workability

The above results indicate that some water in LWA has been released before setting. In the previous study, the desorption behavior of SAP could be evaluated by comparing the rheology [18]. In order to evaluate the water desorption of LWA in UHPC mixture, the workability of UHPC mixtures with and without LWA were measured. It can be observed from Figure 14 that the slump flow changes complexly with function of time. Firstly, both slump flow curves increase during the first 30 min, which is attributed to the delay dispersion of superplasticter [50]. After that, for reference UHPC, the slump

flow decreases gradually due to hydration [51]. However, the sample with LWA shows an opposite trend compared to the reference sample. Although the hydration is adverse to the workability of UHPC containing LWA, the slump flow still shows an unexpected increasing trend in the following 2 h. The slump flow increases from 225 mm to 290 mm when the age proceeds from 5 min to 180 min. Meanwhile, the slump flow reaches to the maximum value at 150 min and then decreases. Apart from water desorption of LWA, it seems that there is no other reason leading to the increase of slump flow. Therefore, it should be concluded that a large amount of water is released during first 3 h, which increases the water to binder ratio of UHPC. As a result, the workability increases with the curing age.

In order to obtain the amount of water that released before setting, the slump flows of UHPC with water to binder ratios of 0.185, 0.19, 0.195, 0.20, 0.205 and 0.21 were tested at different ages. The results tested at 180 min are shown in Figure 15. The slump flow increases with the increasing water to binder ratio. The relationship between slump flow and water to binder shows a linear relation. An equation describing the relationship between slump flow and water to binder ratio is given as following.

$$S=2123.6w/b-141.53 \qquad R^2=0.983 \qquad (1)$$

where S is slump flow (mm); w/b is water to binder ratio of UHPC.

As the addition of LWA has little influence on the initial workability, the evolution of slump flow is mainly due to the water desorption. The water desorption of internal curing materials could be evaluated by comparing the rheology [18]. In this study, the

workability is used to quantify the amount of water desorption. From the relationship between slump flow and water to binder ratio, the slump flow of UHPC reaches 290 mm when approximately 0.0203 extra water is added. This means that 49.4% of pre-soaked water in UHPC releases during the first 180 min. From the development of internal RH, the RH of UHPC with LWA is very high and keeps stable after 3 h. Meanwhile, the heat flow is slowly between 3 h and 6 h (shown in Figure 8). So, the water desorption between is expected to be little. Because it is difficult to obtain the amount of water released between 3 h and final setting time, the 49.40% of water released during the first 180 min can be identified as the water that is not for internal curing (the actual value is certainly higher than 49.40%). Therefore, the water released before setting accounts for high percent of total extra water, more attention should be paid to reduce the influence of this water.

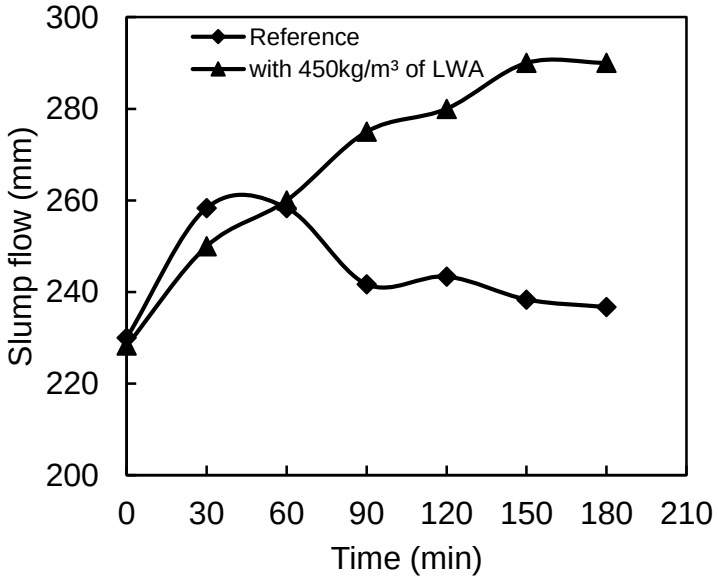


Figure 14 The slump flow of UHPC mixture with and without LWA

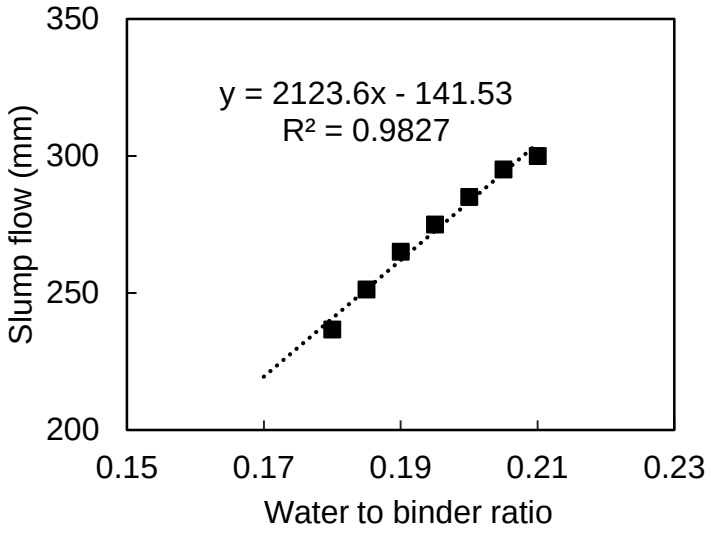


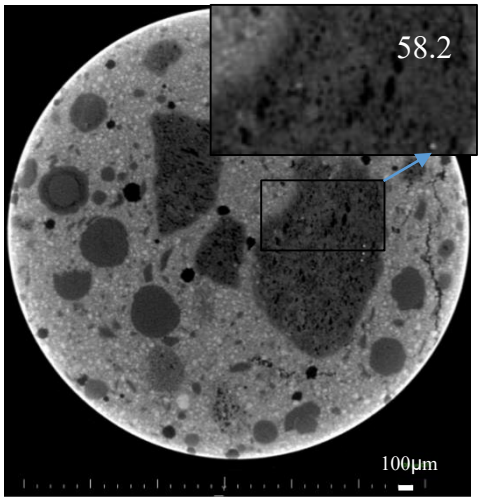
Figure 15 The effect of water to binder ratio on the slump flow of UHPC

3.3.4 In-situ observation of water desorption of LWA in UHPC

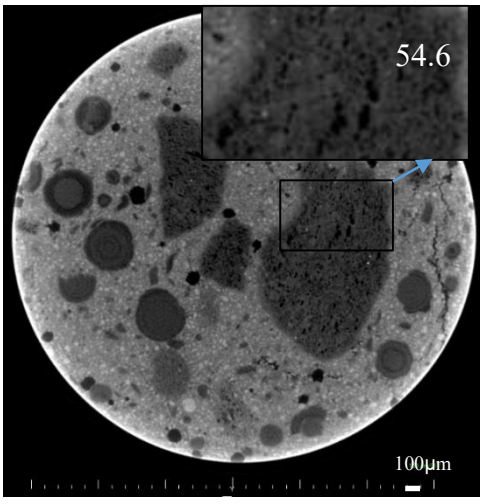
The micro X-ray CT scanner was used to determine the water desorption of LWA. As both air voids and free water in concrete contribute to the porosity peaks [52]. The CaI solution was used to distinguish pores containing free water from empty pores. The samples were tested at 6 h, 12 h, 24 h and 7 d. The 2D-images at different ages for the same position of UHPC are shown in Figure 16. The resolution ratio of this test is 0.7μm/voxel. The CaI solution possess a higher grey level than water, so the grey level of saturated pores in LWA is larger than 50. Usually, the grey level of empty pores is below 46 [53]. It can be observed in Figure 16(a) that there are many large pores being empty at 6 h, which indicates much water has been desorbed during the first 6 h. Furthermore, the water in fine pores of LWA release quickly in the following time. As the presence of CaI solution, the grey level of some parts of saturated pores is higher than empty pores, the average grey level of LWA is about 58.2 (calculated from 100 points in LWA) at 6 h, shows significant difference from empty pores. The average grey

level is rapid decreased to 45.5 at 24 h, representing large amount of water in LWA has released. However, the development of average grey level slows down from 24 h to 7 d, and little difference can be obtained by calculating average grey level. Therefore, most of water in LWA has been desorbed during the first 24 h, after that there is little water remained in LWA. Also, it should be noticed that some CaI crystals are separated out in LWA at 7 d.

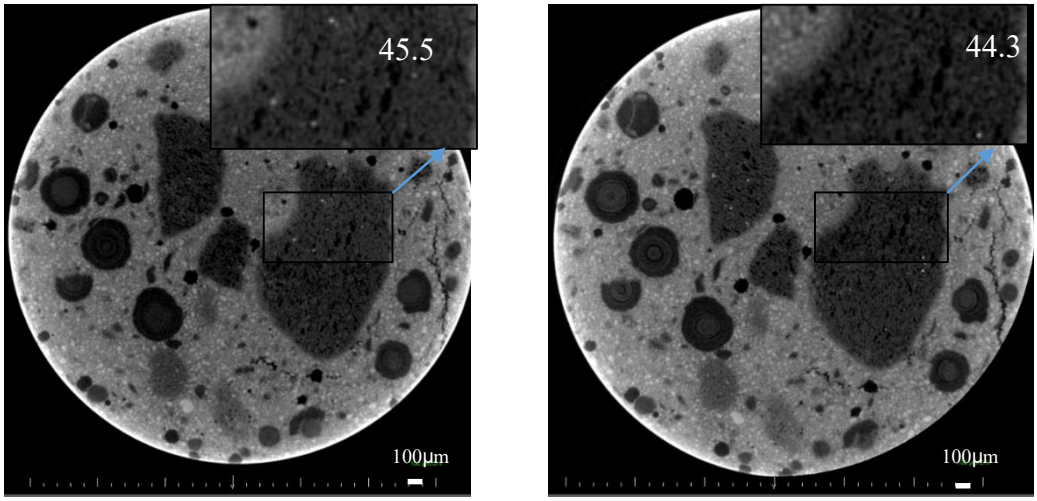
On the basis of the above qualitative observation, the slices obtained using tomography is an effective in situ method to indicate the water desorption of LWA. It can be concluded that the water in large pores of LWA desorbs rapidly before setting. So many large pores are empty at 6 h. The water in fine pores desorbs quickly during the period between 6 h and 24 h, and most of the water in LWA is already desorbed during the first 24 h. But these images from the same place of UHPC also illustrate the difficulty to achieve the transport process of moisture in cement paste and the actual remained water in LWA.



（1）6h



（2）12h



（3）24h （4）168h

Figure 16 The micro-CT images of UHPC at different ages

3.3.5 Chemical shrinkage and autogenous shrinkage

As the water stored in LWA has been released before setting, the initial water to binder ratio of UHPC containing 450kg/m^3 of LWA is equal to about 0.203. Therefore, the UHPC with the water to binder ratio of 0.203 was prepared to determine its chemical shrinkage and autogenous shrinkage. The test results are shown in Figure 17. From the development of internal RH shown in Figure 7, the RH in UHPC containing LWA indicates that the capillary pores keep saturated for about 40 h. About 0.017 water to binder ratio is needed to fill into the void space created by chemical shrinkage. As the pores in UHPC are still nearly saturated at 40 h in UHPC containing 450kg/m^3 of LWA, the water released during the period between 6 h and 40 h is mainly used to fill in the pores created by chemical shrinkage. Considering the water desorption before setting, there is at least 0.04 extra water to binder ratio has already released at 40 h. In other words, about 85.10% water stored in LWA has been released before 40 h. These results

are different from result obtained from thermal-humidity test chamber. Although the RH gradient is one of the most important factors that should be considered, the actual water desorption depends on many other factors such as pore structure and LWA content [54, 55].

According to previous study, as for ordinary and high performance concrete, the volume fraction of water migrating from LWA exhibited a one-to-one agreement with the measurement chemical shrinkage of cement paste [54], the water in LWA is completely used for internal curing. But for UHPC, nearly half of the water stored in LWA is not for internal curing. This may be the main difference between water desorption in UHPC and that of other concrete with high water to binder ratio.

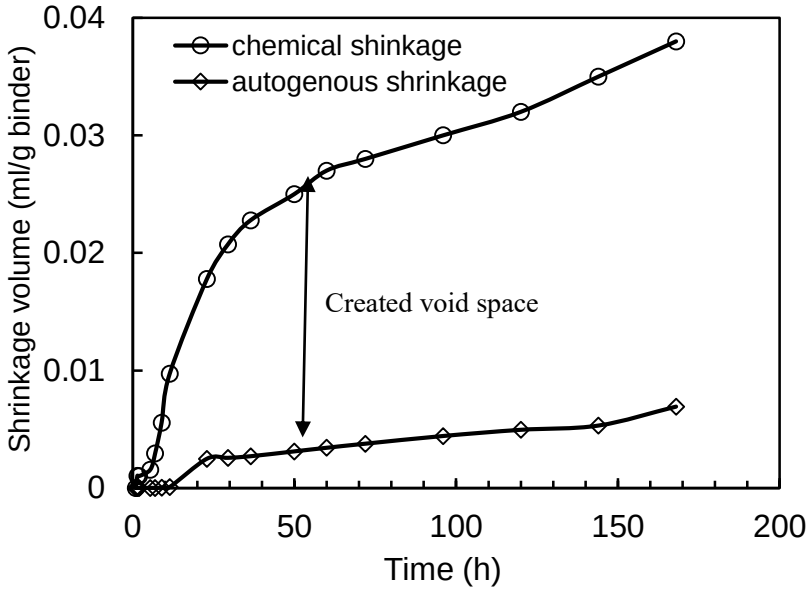


Figure 17 The chemical shrinkage and autogenous shrinkage of UHPC

4. Further discussion

4.1 Characteristic water desorption of LWA in UHPC

Based on the experimental results, the water desorption process of LWA in UHPC can be divided into 4 stages (shown in Figure 18). In the first stage, the saturated LWA is surrounded by UHPC mixture with low RH, and the water releases with high rate. This water desorption occurs before setting, which improves the initial water to binder ratio of UHPC. Because the UHPC is still mixture, the water desorption is mainly controlled by RH gradient. In the second stage, the internal RH is very high and the pores in matrix is nearly saturated, and the hydration rate is still slow. The UHPC is in the state of mixture, and no self-desiccation can be found, so the water desorption is slow, which shows limited influence on the water to binder ratio and hydration. In the third stage, it starts after the time of final setting, the water releases into the matrix and is used for internal curing. The RH keeps high during this period due to water desorption. But the water consumption of hydration is rapidly, leading to quick water desorption of LWA. The water desorption is possible to be motivated by capillary pressure rather than RH gradient, which is due to the relatively high and constant RH. In the fourth stage, most of water stored in LWA has been released. As the internal RH decreases with the increasing curing age. Apart from the RH gradient, the capillary pressure is very high, which promotes the desorption and migration of water in LWA. However, the porosity and connectivity of capillary pores in UHPC is continuously reduced [27], so the water

desorption and migration is gradually slowed down. So, there are three main factors controlling the water desorption of LWA in the fourth stage: internal RH, capillary pore pressure and pore structure.

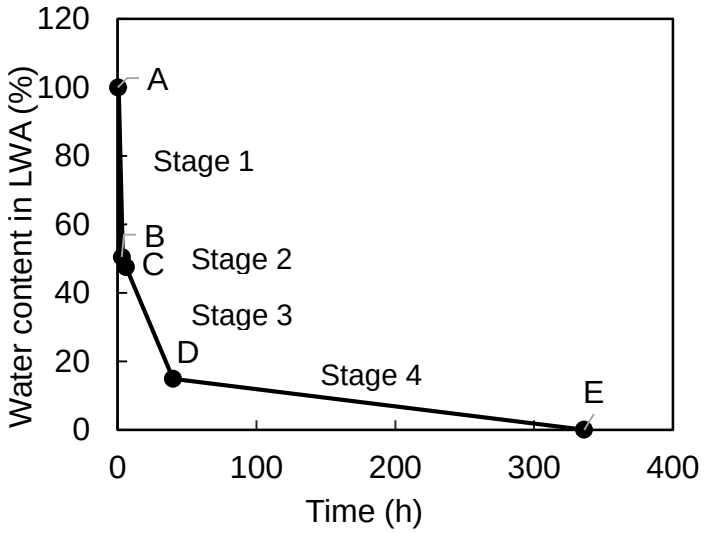


Figure 18 A characteristic desorption curve of LWA in UHPC

As is known to all, the pore structure of capillary pores in hardened concrete are closely related to the initial water to cement ratio and hydration degree [49]. Much water in LWA has been release before setting due to the very low water to binder ratio. This free water increases the initial water to binder ratio of UHPC which may be adverse to the mechanical strength and permeability of UHPC. This is usually mostly unexpected. If the water releases at too early age, for example, during the first stage, this free water is not for internal curing. Considering the internal curing effect of LWA, the water stored in LWA is expected to be released less in the first stage and more in the third and fourth stage, so that the LWA can bring better internal curing efficiency. Therefore, a kind of LWA with fine pore size may improve the internal curing efficiency. Because the water in coarse pore would release easily at high internal RH and low RH

gradient [24].

Nevertheless, the water desorption process of LWA in UHPC is individual due to the very low water to binder ratio and large amount of superfine powders. The water desorption behavior of LWA in UHPC is significantly different from that of normal concrete [36], and it can be showed as follows: Firstly, much water stored in LWA has been released before setting; Secondly, the water in LWA is released rapidly between 6 h and 24 h, and most of the water has been released during the first day of hydration.

Based on the above analysis, the desorption process of LWA in UHPC is plotted in Figure 18. There are three inflection points at 3 h, 6 h and 40 h for UHPC containing 450kg/m^3 of LWA. These three inflections are denoted as B, C and D, respectively. These three inflection points are related to the setting time of UHPC, the content and characteristic of LWA and mix proportion of UHPC. This curve is plotted as a linear line in each stage. However, every stage is not linear due to the evolution of RH and pore structure. Among these four stages, the water released during the first and second stage is not used for internal curing.

4.2 The utilization rate of the internal curing water

It can be observed from Figure 18 that the water desorption during the first and second stage is used to increase the water to binder ratio, which is not used for internal curing. As the water desorption in the second stage is slow due to high internal RH. The released water that is useless for internal curing refers to the water desorption in the

first stage (shown in Figure 18). It can be obtained from Figure 13 that much water has been released at 180 min, and an equation describing the relationship between slump flow (at 180 min) and the real water to binder ratio is given. Meanwhile, the addition of LWA has little influence on the initial workability of UHPC. If the slump flow (at 180 min) and initial water to binder ratio are known, the additive water to binder ratio can be obtained by real water to binder ratio minus initial water to binder ratio. Therefore, the water desorption in the first stage can be known. Here, the utilization rate (U_{ic}) of internal curing water of LWA is referred to the ratio of water desorption except the first stage to total pre-soaked water. The workability of UHPC containing different dosages of LWA is tested (shown in Figure 19) to calculate the utilization rate of internal curing water.

The U_{ic} of UHPC containing 450kg/m^3 of LWA is 50.6%, which is calculated based on the development of workability and Equation (1). Actually, the water to binder ratio and LWA content would influence the utilization rate. Figure 20 shows the effect of LWA content on the utilization rate of water stored in LWA. It can be observed that the utilization rate is very low for a low content of LWA (150kg/m^3), most of the water in LWA has been released during the first stage. Although more water is introduced to UHPC when more saturated LWA is added, the proportion of water released in the first stage decreases with the increasing LWA content. In others words, the utilization rate is improved as the increasing LWA additions. The utilization rate of samples with 150kg/m^3, 300kg/m^3, 450kg/m^3 and 600kg/m^3 of LWA are 27.35%, 42.56%, 50.60%

and 55.70%, respectively. This means that more water stored in LWA is released in sample with higher LWA content during the third and fourth stages. However, it should be noted that different additions of LWA in this study cannot meet the required theoretical water amount, so even 75% LWA would not be enough for shrinkage compensation [19]. For all the samples, no matter how much LWA is present, much water will be released before setting, which increases the workability and water to cement ratio. This is adverse to the microstructure and mechanical performance of UHPC. A higher U_{ic} is found in sample with higher LWA content. Also, it can be observed in Figure 14 and 16 that much water has been released at early age, and the coarse pores are empty at 6 h. In order to further improve the U_{ic}, improving the LWA additions and reducing the pore size of LWA both contribute to achieving the theoretical water necessary, improving the internal curing efficiency and preparing non-shrinkage UHPC.

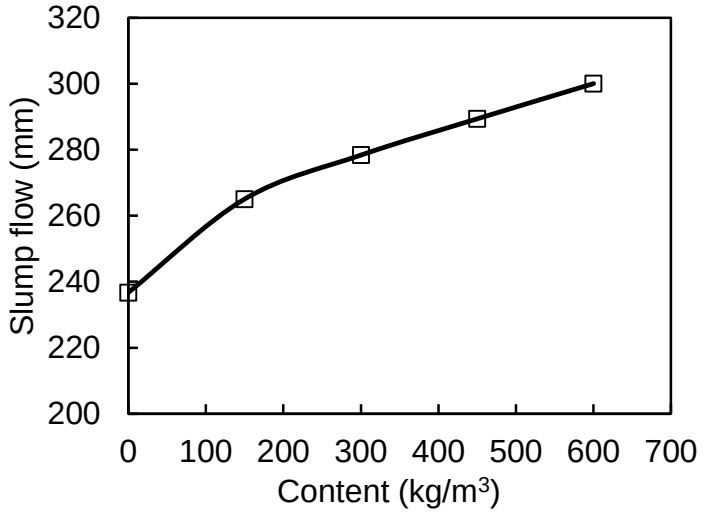


Figure 19 The effect of LWA content on the workability of UHPC

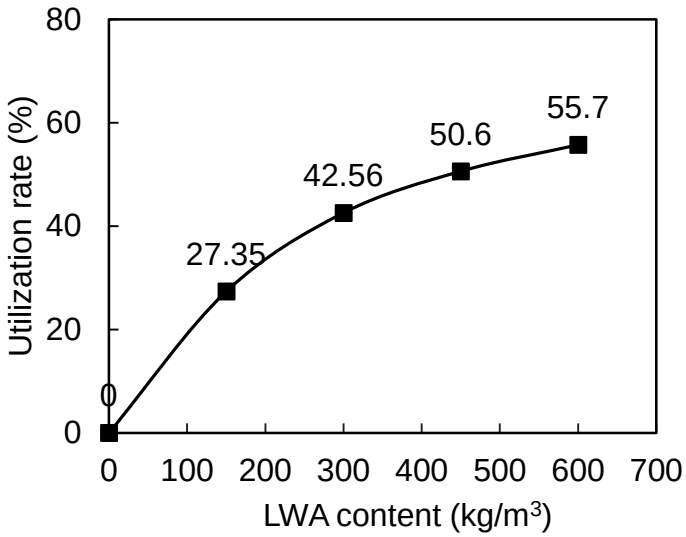


Figure 20 The utilization rate of internal curing water of LWA in UHPC

5. Conclusion

A comprehensive investigation of water desorption characteristics of saturated lightweight fine aggregate in ultra-high performance concrete is presented. The water desorption characteristics of LWA in UHPC and its effect on the hydration and microstructure are systemically investigated. Based on this experimental investigation, the following conclusions can be drawn.

(1) The LWA used in this study possesses a large porosity, which can absorb large amount of free water. Most of the pores are larger than 100 nm, which leads to a rapid water absorption and easy water desorption at high RH. This indicates that the LWA is an efficient aggregate which is available for the internal curing of the cementitious materials.

(2) The water desorption of LWA improves the internal RH not only at early age but also at later age. Some water is released when the UHPC is still in the state of mixture due to the low internal RH. As a result, although the hydration rate and

hydration degree of UHPC are both obviously improved, the pore structure is deteriorated leading to the reduction of compressive strength at early age. However, as the water desorption proceeds, this adverse effect is overwhelmed by the effect of internal curing of LWA.

(3) Much water desorbs rapidly before setting due to the very low water to binder ratio. The water also desorbs quickly between 6 h and 24 h, and most of the water has been already released during the first day. For sample containing 450kg/m^3 of LWA, there is about 85% of pre-soaked water in LWA which has been released before 40 h, and at least 49.4% of presoaked water is not for internal curing. The water desorption of LWA is not only controlled by RH gradient but also other factors such as pore structure and LWA content.

（4）A “four-stage desorption” mechanism driven by capillary pressure and RH gradient is proposed in the study. This process can be divided into 4 stages: the first and second stages occur before setting, which is mainly motivated by RH gradient; The water desorption in the third and fourth stages is used for internal curing. The water desorption that is beneficial for the internal curing is calculated. It is indicated the internal curing efficiency could be enhanced by increasing LWA content and reducing pore size.

Acknowledgements

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