Internal curing of high performance concrete using cenospheres

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ABSTRACT

This study explores a novel internal curing agent, perforated cenospheres. Cenospheres are hollow fly ash particles produced from coal burning power plants. The shell of the cenospheres is inherently porous that is sealed by a thin layer of glass-crystalline film. By removing this film through chemical etching, the pores on the shell can be exposed, perforating the cenospheres and providing paths for water propagating into the internal volume of cenospheres. The perforated cenosphere were found to have water absorption as high as 180 wt.%. The loaded water can be readily released from the cenospheres under high relative humidity (95%). When incorporating saturated cenospheres into cement mortar for internal curing, the autogenous shrinkage of the mortar was almost eliminated. The internal curing also improved the compressive strength of the cement mortar. All these results suggest that perforated cenospheres can be used as an efficient internal curing agent for HPC.

Keywords: Internal curing, High performance concrete, Cenospheres, Autogenous shrinkage, Early-age cracking

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1. Introduction

Autogenous shrinkage is an important phenomenon in early age concrete, in which water can be rapidly drawn into the hydration process and the demand for more water creates very fine capillaries. The surface tension within the capillaries causes autogenous shrinkage which can lead to premature cracks, making the concrete more vulnerable to the ingress of potentially aggressive species and thus severely reducing the durability of concrete. Early age cracking due to autogenous shrinkage is especially serious for high-performance concrete (HPC) because of its low water to cement ratio [1]. These cracking problems cannot be mitigated through conventional full water curing due to HPC's compact structure and very low permeability. To combat this problem, internal curing method has been developed in which water-filled internal curing agents are added to concrete mixture. These internal curing agents are used as water reservoirs which can gradually release its water during the hydration process. The released water can maintain a high relative humidity inside the concrete pores to prevent self-desiccation in concrete [1]. As a result, autogenous shrinkage of concrete can be reduced or eliminated, which will ultimately minimize cracking and significantly promote the durability of structural concrete [2,3]. More complete cement hydration is also achieved by internal curing due to extra curing water provided by the internal curing agent, creating a denser cement paste, reducing permeability [1,4,5]. As a result, the service life of concrete structures can be significantly increased and the life-cycle cost can be significantly reduced [6].

The key element in internal curing technique is to choosing a proper internal curing agent to load and release water in concrete as needed. An ideal internal curing agent should release most of its absorbed water uniformly at high relative humidity within an appropriate time [1] in order to optimize internal curing of concrete [7]. The most often used internal curing agents are pre-

wetted high porosity lightweight aggregates (LWAs) and super absorbent polymers (SAPs) [1]. LWAs include lightweight coarse aggregates (LWCAs) with a particle size greater than 6.35 mm and lightweight fine aggregates (LWFAs) with a particle size smaller than 6.35 mm. Pre-wetted LWFAs are more suitable than LWCAs because of two reasons [8]: 1) LWFAs can produce better distribution of moisture; and 2) LWCAs don't have the approximate gradation of the natural aggregate being replaced. SAPs can expand to absorb thousands of times their dry weight in water without dissolving, although commercially available SAPs generally exhibit absorbency below 20g/g. When used in cement to entrain water, the high pH environment of the concrete mixture can substantially reduce the absorption extent of SAPs compared to pure water. Nevertheless, the SAPs can absorb much more water to be used in internal curing than LWAs.

Although great success has been achieved by these two internal curing agents, they can be further improved to minimize the adverse effect on the mechanical properties [9,10] induced by the internal curing agents. This is because in nature the internal curing agent is much weaker than normal aggregates. To this end, the amount of necessary internal curing agent should be minimized [7]. By using the concept of protected paste volume, Bentz and Snyder [11] found that cement paste should lie within a sufficiently small distance from the internal curing water reservoir so that the internal water could penetrate. Within this distance, the cement paste is protected by the internal curing water from self-desiccation. Clearly, smaller spacing between internal curing agent particles is more desirable because more cement paste can be protected by the internal curing water. To achieve this, the internal curing agent particle size should be as small as possible [7]. Some experimental studies [12] did show that smaller internal curing agent particles perform better than the larger ones. Zhutovsky et al. [13] also found that reduction of the internal curing particle size down to 4–2 mm can improve the curing efficiency. However,

further reduction of the internal curing agent particles led to reduction of internal curing efficiency, instead of increase. Zhutovsky et al. [7] found that this apparent discrepancy was caused by two competing mechanisms taking place upon reduction of the particle size of the internal curing agent: i) small spacing factor can increase the internal curing efficiency; while ii) small particles have smaller pores which tend to hold water more tightly, making them unavailable for internal curing. When the particle size is sufficiently small, the second mechanism overrides the first mechanism, leading to reduction in internal curing efficiency. Therefore, to obtain optimal internal curing result, only reducing the spacing between particles is not sufficient. The structure of the internal curing agent particles must be optimized too. To make water more available to internal curing, the size of the pore in the internal curing agent particles should be as large as possible. Theoretically, the largest size for a pore should be the size of the particle itself. However, the currently used internal curing agents, neither LWAs nor SAPs can have such a pore structure.

In this study, a novel internal curing agent with such an optimal pore structure, perforated cenospheres is proposed for internal curing of HPC. Cenospheres are hollow fly ash particles generated in coal burning power plants, which have sizes ranging from a few to hundreds of micrometers (Fig. 1(a)). Cenospheres are much smaller than LWAs, thus they can provide better distribution of curing water. Since they have only one large pore, which is very close to their own size, as shown in Fig. 1(b), water can be loaded into and released from them easily. Moreover, cenosphere particles have an aluminosilicate shell with high stiffness and strength and a thickness of just a few micrometers. The potential of using cenospheres to deliver water was noticed by Jensen and Lura [14] 10 years ago. They stated that “If water-filled, the capsule wall (of cenosphere) could have beneficial pozzolanic properties whereas the water might serve as

internal curing water.” However, they have never been implemented because the shell of cenospheres is covered by a glass-crystalline nanosize film (Fig. 1(a)). Without removing this thin film, the inner volume of the cenosphere is inaccessible to water, as shown in Fig. 1(a). Jensen and Lura [14] also pointed out that “no method to induce the water into the particles or to ensure its proper release when needed seems to be available.”

In this work, this barrier has been removed through removing the thin film by a simple chemical etching process. Water can then be easily induced into or released out of cenospheres through the holes perforating the shell of the cenospheres. It is found from this research that perforated cenospheres have a water absorption as high as 180 wt.%, and the loaded water can be readily released from cenospheres under high relative humidity of 95%. When mixing the saturated cenospheres into mortars, the autogenous shrinkage can be eliminated without compromising the compressive strength. These findings suggest that the perforated cenospheres have a great potential to be used as an efficient internal curing agent for HPC.

Fig. 1. Microstructure of cenospheres under SEM observation: (a) a cenosphere with impermeable shell; (b) porous shell of the cenosphere.

2. Materials and Methods

2.1. Materials

In current study, reagent grade ammonium fluoride (NH_4F) and hydrochloric acid (HCl) were used. Calcium gluconate gel was always present during handling of hydrofluoric based acid solution (1.0 M NH_4F -1.2 M HCl - H_2O).

Cenospheres used have sizes between 10 and 200 μm . Table 1 shows the chemical composition of cenospheres, gained by X-ray fluorescence (XRF) analysis. The composition of Type I Portland cement used for casting mortar is also listed in Table 1. It has to be pointed out that XRF technique can provide excellent quantification for many elements in the periodic table except those with low atomic weights, e.g., oxygen. In an effort to compensate for the matrix effects of the compounds routinely compromising the solids, the XRF software offers the option to represent the elemental concentrations as oxides. For cement-based materials, comparing and contrasting ‘oxide equivalent’ within a sample can provide a more helpful and representative metric relative to a comparison of elemental concentrations [19,20,27]. Thus in this paper, the XRF data is reported as oxide compositions.

2.2. Production of perforated cenospheres with acid etching

Cenosphere particle has an aluminosilicate shell with a thickness in a few micrometers (Fig. 1(a)). The shell has a porous structure formed by gas inclusion and is covered by a glass-crystalline nanosize film, which is shown in Fig. 1(b). To make the internal volume of cenospheres accessible for water, the film should be removed. This can be done by etching the cenospheres with acids [15]. Approximately 12 g of cenospheres were soaked into 250 mL of 1.0 M NH_4F -1.2 M HCl - H_2O solution for 2 hours with occasional stir. By the end of this treatment, more than 95% of cenosphere sank to the bottom of container, which were floating on the

surface of acid solution at the beginning. The settlement of cenospheres indicates the completion of perforation. After etching, the perforated cenospheres were vacuum filtered and rinsed with 1500 mL of water, followed by being dried in an oven at 110 °C.

The morphology and microstructure of as-received (Fig. 1) and the produced perforated cenospheres were investigated using a JOEL 7000 FE scanning electron microscope (SEM). The microscope was operated at low accelerating voltage (1~3 kV) and 10 mm working distance with a spot size of medium 8. Before being put into SEM chamber, cenospheres were coated with a layer of gold, in order to mitigate the charging effect.

Table 1. Chemical composition of cenospheres and Type I Portland cement

Compound	As-received Cenospheres, %	Type I Portland Cement, %
SiO ₂	57.35	22.93
Al ₂ O ₃	31.93	4.68
CaO	0.44	64.04
Fe ₂ O ₃	2.27	2.41
TiO ₂	1.17	0.20
MgO	0.54	3.38
Na ₂ O	0.54	0.23
K ₂ O	1.40	0.76
P ₂ O ₅	0.06	0.08
MnO	N/A	0.07

2.3. Absorption and desorption behaviors of perforated cenospheres

Determination of the water absorption was obtained by measuring the weight difference between the oven dry and saturated surface dry (SSD) cenospheres. The procedures of obtaining SSD cenospheres were based on the ASTM C128 [16]. Water can be loaded into perforated cenospheres simply by mixing them together. When cenospheres all sank down to the bottom of the water container, the loading of cenospheres with water was completed. The saturated cenospheres were then filtered and placed in a cone slightly tamped for 25 times, and the cone

was removed. The cone tests rely on the principle of surface tension for determining when the surface moisture disappears. When the moisture is still on the surface of the cenosphere, surface tension of the water will hold the particles in the form of the cone after the cone is removed. When no moisture is present on the surface, slight slumping of the cenosphere cone will occur, which means the cenospheres achieve the SSD condition. Then the SSD cenospheres were collected and weighted. Thereafter, they were dried in an oven at 110 °C for 48 hours to calculate the absorbed water percentage, which was found to be around 180% by weight of the oven dry cenospheres.

When used for internally curing the concrete, water loaded in cenospheres has to be readily released to the surrounding cementitious matrix under high relative humidity. Thus, a study was conducted to evaluate the water release behavior of the cenospheres under two different relative humidity (RH) levels: 95% and 50%. The RH of 95% and 50% simulate the moisture condition in the cement paste at the very early and late ages, respectively. In addition, these two humidity levels could also represent the moist environment under the moist and air curing, as specified in ASTM C511 [17]. The oven-dry, perforated cenospheres were placed in water first. When the cenospheres sank at the bottom of the container, they were removed from water by vacuum filtering. At this point, the saturated cenospheres were obtained. Thereafter, SSD cenospheres are obtained by the applying the cone test as described above. Then a 5.0 ± 0.0001 g of SSD cenospheres were placed in a tarred quartz pan with a diameter of ~ 15 cm. The pan containing the sample was then suspended from the balance (± 0.0001 g accuracy) and placed in a relative humidity chamber to equilibrate at 23 ± 1 °C and 50% or 95% relative humidity until the sample had achieved a stable mass (mass change is less than 0.0001 g/15 min). The weight of the sample

was recorded at an interval of 15 minutes. After equilibrating, the samples were dried at 110 °C for 48 hours to calculate the dry weight of the perforated cenospheres used.

2.4. Vicat needle measurement

Saturated cenospheres were integrated into cement paste to evaluate the effect of internal curing on the setting time of cement paste. The pastes had a w/c ratio of 0.35, which fell into the range of w/c ratios for high performance concrete (0.45~0.21) [18–20]. Addition of saturated cenospheres was designed to provide 9% of internal curing water by weight of cement, corresponding to 5% of oven-dry, perforated cenospheres that have a water absorption of 180 wt.%. This amount of internal curing water was appropriate for compensating the moisture loss caused by cement hydration [1,21]. For comparison purpose, setting time of control paste samples was also studied, including those without any cenospheres and with 5% of nonperforated cenospheres.

All the cement pastes were mixed according to the ASTM C305 [22]. For the cement paste with internal curing, the weighted oven-dry, perforated cenospheres were saturated with the total amount of mixing and internal curing water first. After all the perforated cenospheres has been settled down to the bottom of water container, the mixture was then mixed with cement to prepare the cement paste. The control samples were prepared by directly mixing the dry materials and water together.

The initial and final setting time of cement paste were determined by the Vicat needle tests, which were carried out according to ASTM C191 [23]. When the needle penetrated into the cement paste for 25 mm, initial set was achieved. Final setting was attained when there was no mark of the specimen surface with a complete circular impression. The tests on the control and internally cured samples were repeated 3 times to ensure the precision of the determination.

2.5. *Effects of internal curing on heat evolution*

Isothermal conduction calorimetry was also implemented on the cement pastes with a w/c ratio of 0.35, based on ASTM C1702 [24]. For the internally cured pastes, dry perforated cenospheres was added in the amount of 3.33% and 5% by weight of cement, providing 6% and 9% additional water for internal curing, respectively. As it is known that typically the internal curing water does not exceed 6% by weight of cement used [20,21]. But it could also be interesting to examine whether extra water provided by cenospheres beyond 6% can further improve the internal curing efficiency or not. Thus in addition to the 6%, the effect of providing 9% internal curing water was also studied. Control samples without any cenospheres or with 5% nonperforated cenospheres were also tested for their heat signatures.

An Isothermal calorimeter (I-Cal 2000 HPC Isothermal Calorimeter) was employed to monitor the heat evolution in all the cement pastes. Before testing, the calorimeter was regulated at constant temperature of 22 ± 1 °C and then equilibrated for 24 hours. All the cement pastes were mixed by pan mixer and cast into a plastic cup that is specially crafted to fit the calorimeter channels. Each sample contained 50.0 g of Portland cement. The freshly mixed cement pastes were promptly placed into the channels of the calorimeter. The heat evolution within 7 days after mixing was recorded continuously. It should be mentioned that external stirring of cement paste will lead to non-meaningful heat of hydration during the very initial period. Therefore, integration of the accumulative heat was started from 20 minutes so that the error in the initial period could be minimized.

2.6. *Internal curing efficiency of perforated cenospheres*

Saturated cenospheres were integrated into cement mortar to evaluate its internal curing efficiency in terms of mortar's autogenous shrinkage and compressive strength. The mix

proportions are listed in Table 2. There were four mix proportions used, the control mortar without cenospheres (Control_0%) or with 5% nonperforated cenospheres (as-received cenospheres) (Control_9%), the mortar with 6% internal curing water by weight of cement (IC_6%), and the mortar with 9% internal curing water (IC_9%). The amount of superplasticizer was adjusted for obtaining the similar workability for the four mixes. It can be seen from the table that cenospheres are not included as cementitious material in the mixes. Instead, they replace some volume originally occupied by sand in the control sample without cenospheres. The inclusion of cenospheres slightly reduces the water to binder (w/b) ratio of the mortar if the cenospheres are treated as binder. Nevertheless, this will not interfere with the analysis of the effect of internal curing on the mortar properties because internal curing water participates in cement hydration at early age when pozzolanic reaction of cenospheres is minimal.

Table 2. Mix proportion of mortar (kg/m³)

Constituent	Control 0%	Control 9%	IC 6%	IC 9%
Cement	592.0	592.0	592.0	592.0
Water	207.2	207.2	207.2	207.2
Sand	1539.2	1432.6	1468.9	1432.6
Nonperforated cenospheres	-	29.6	-	-
Perforated cenospheres	-	-	19.5	29.6
Internal curing water	-	-	35.2	53.3
Superplasticizer	3.0	3.0	1.8	1.8

For control mortars without internal curing (Control_0% and Control_9%), fine materials (cement and/or unperforated cenospheres), water, and sand were mixed homogeneously according to the ASTM C305 [22]. For the mortars with internal curing, the perforated cenospheres were first mixed with calculated weight of water (both internal curing and mixing water) to be saturated. Then the mixture was mixed with cement and sand together following the

ASTM C305 [22]. After mixing, each mortar was cast into molds for the measurements of autogenous shrinkage and compressive strength.

The autogenous shrinkage of the mortar was measured by an automated testing system shown in Fig. 2, based on ASTM C1698 [25]. The mortar was cast into the molds consisting of corrugated plastic tubes, having a length of 420 ± 5 mm and an outer diameter of 29 ± 0.5 mm. The small diameter of the molds limits the temperature differences that may arise during hydration of the cementitious materials. As stated in the standard [25], the typical maximum temperature increase in the center of test specimen, due to heat of hydration of mortar has been determined to be 2°C . In addition, the mortars were stored under the controlled laboratory condition with constant temperature of $23.0 \pm 1.0^\circ\text{C}$ all the time. Based on all these, it can be assumed that the deformation caused by thermal stress due to cement hydration is negligible, and it is validate to take the measured length change as autogenous shrinkage. The automated testing system measured the sample length continuously after final setting till 7 days with an interval of 10 minutes.

Fig. 2. Automated version of ASTM C1698 (2014) to measure the autogenous shrinkage of cement paste.

For the compressive strength test, the mixed mortar was cast into 50×100 mm cylindrical molds and compacted using a vibration table. After 24 hours, the samples were demolded and

put into plastic bags for sealed curing at a controlled temperature of 23 ± 1 °C till the designated ages of 3, 7, and 28 days. At each age, compression test was carried out on three samples according to the ASTM C109 [26]. The mortar samples were crushed into pieces with appropriate size for SEM observation as well.

3. Results and discussion

3.1 Microstructure of perforated cenospheres

The original cenospheres represent a silicate-alumina-iron multiple component system with the surface covered by glass-crystalline nanosize film (Fig. 1(a)). After acid etching with 1.0 M NH_4F -1.2 M HCl - H_2O for 2 hours, this film was removed as shown in Fig. 3. Small holes with size smaller than 2 μm penetrating through the shell were introduced on the surface of the cenosphere shell by the acid etching, through which water can be easily loaded into the hollow particles. The porous structure of the shell of the cenosphere shown in Fig. 1(b) makes the chemical etching extremely efficient since only the film covering the pores on the shell needs to be removed.

Table 3 lists the chemical composition of cenospheres after acid treatment. Comparing with the original composition (Table 1), the content of alumina was increased from 31.93 to 35.00% in the perforated cenospheres. This is because alumina was not subjected to the etching action [15], while the silica and iron deposits on cenospheres were dissolved by the hydrofluoric based acid system. The dissolution resulted in about 8.77% weight loss of the cenospheres shell.

Fig. 3. SEM microphotograph of the perforated cenospheres after being etched with 1.0 M NH_4F -1.2 M HCl - H_2O solution for 2 hours.

Table 3. Chemical composition of perforated cenospheres produced by acid etching

Compound	Perforated cenospheres, %
SiO_2	57.81
Al_2O_3	35.00
CaO	0.33
Fe_2O_3	2.13
TiO_2	1.15
MgO	0.51
Na_2O	0.52
K_2O	1.32
P_2O_5	0.05

3.2. Desorption behavior of perforated cenospheres

The perforated cenospheres were mixed with water. After all of them had settled at the bottom of the water container, cenospheres were filtered and SSD cenospheres were obtained through the method described in Section 2.3. These cenospheres were studied for their water desorption behavior under the two different RH levels. The results are shown in Fig.4. In the environmental chamber with RH of 50%, the SSD cenospheres achieved equilibrium in 10 hours, which took around 24 hours under RH of 95%. And at equilibrium, about 99.7% and 90.6% of

loaded water was released from cenospheres under the RH of 50% and 95%, respectively. This could serve as a good foundation for taking cenospheres as internal curing agent, since most of the autogenous shrinkage in Portland cement paste was found to occur from the moment of final setting to 2~4 days after mixing [1,20,27]. From the rate point of view, the water release from cenospheres could promptly compensate for the self-desiccation which causes autogenous shrinkage at the very early age.

Fig.4. Water release behavior of the perforated cenospheres at RH levels of 50% and 95%.

3.3. Setting time and heat evolution

The saturated cenospheres were incorporated into cement paste to evaluate the effect of internal curing on the hydration process as reflected by setting time and heat evolution. Fig.5 shows the penetration curves for both control and internally cured pastes. Based on these curves, the initial and final setting time are found to be 2.2 h and 5.9 h for sample without cenospheres (Control_0%), 3.3 h and 7.1 h for sample with 5% nonperforated cenospheres (Control_9%), and 3.8 h and 8.0 h for internally cured sample (IC_9%). These indicate that setting of paste is slightly extended by the inclusion of nonperforated cenospheres, which is further retarded in the internally cured sample. With the inclusion of 5% nonperforated cenospheres, both the initial and

final setting of the paste are retarded by about 1 hour, compared with the control sample without cenospheres. This can be attributed to the dilution effect with the inclusion of cenospheres. Testing of setting time is carried out on cement paste. While keeping the same w/c ratio, the inclusion of 5 wt.% of dry cenospheres occupies a portion of volume that belongs to cement and water, comparing to the control sample without cenospheres. This dilutes the concentration of cement and water proportionally in the tested volume of paste. As it is known that cenospheres are actually hollow fly ash particles that are not reactive at early age. Thus the dilution of cement and water by cenospheres resulted in the slower setting of cement paste. From Fig. 5, further retardation in internally cured pastes is also found and it could be caused by the release of additional water from cenospheres. The similar phenomena were also observed by other researchers [28,29].

Fig.5. Vicat needle penetration curves for the control and internally cured cement pastes.

Fig. 6 plots the measured heat evolution curves for the pastes studied. From Fig. 6(a), two peaks are observed at the time between 7 and 11 hours. The first peak is caused by the reaction of C_3S , while the second peak should be attributed to the reaction between gypsum and more

available aluminate that is from the continuous cement dissolution [30]. It is also found from Fig. 6(a) that the integration of either nonperforated or perforated cenospheres slightly reduce the height of main peaks and shift the peaks to the right, in comparison with the peaks in Control_0%. Peak reduction indicates that maximum heat release rate from cement hydration is lower, while the right shift of the peak means that it takes longer for cement paste to achieve the highest hydration rate. Both of these reveal the slower hydration in the pastes with cenospheres. This corresponds well to the longer setting time in these samples, as seen in Fig. 5. Slower the hydration, longer the initial and final setting will take. The lower peak for the sample of Control_9% could be caused by the fact that some of the mixing water is being used for wetting the surface of the dry nonperforated cenospheres. Less water available for cement to react slows down the heat releasing rate from hydration. Slight reduction and right shift of the main peak for the internally cured samples were also observed by other researchers either using LWAs or SAPs for internal curing [20,29,31].

Fig. 6(b) compares the total amount of heat released from mortar samples with/without internal curing. According to the figure, the heat of hydration from all the mortars is close to each other in the first few hours. Then the hydration proceeds much slower in the control sample with nonperforated cenospheres (Control_9%). As discussed above, this could be caused by the less water available for cement hydration, since part of the mixing water is taken to wet the dry surface of the nonperforated cenospheres, lowering the hydration rate of cement. It is also remarkable that pastes with saturated cenospheres release much higher amount of hydration heat than the control one with only nonperforated cenospheres, even slightly higher than the control sample without any cenospheres. This indicates that the water in the perforated cenospheres is

participating in the hydration reactions. It has also been observed in previous researches that internally cured sample released higher amount of hydration heat than control samples [29,31,32].

(a)

(b)

Fig. 6. Effect of internal curing on (a) the rate of heat evolution and (b) the total amount of heat released during hydration.

3.4. *Autogenous shrinkage of mortars with or without internal curing*

The autogenous shrinkage of the control and internally cured mortars with w/c ratio of 0.35 is shown in Fig. 7. Each sample was measured continuously from their respective final setting till 7 days. Before final setting, autogenous shrinkage will not occur since the mortar is still at the plastic status. According to the shrinkage curves, it can be seen that the two control samples shrink continuously within the measuring frame. The rapid shrinkage continued till 10 hours, after which the samples shrink slowly and gradually. The ultimate shrinkage was around 120 $\mu\epsilon$ for the mortar without any cenospheres and 80 $\mu\epsilon$ for the one integrated with 5% nonperforated cenospheres at 7 days. The smaller shrinkage induced by including nonperforated cenospheres can be due to the less availability of water for cement hydration, since a portion of the water is taken to wet the surface of dry nonperforated cenospheres during mixing, resulting in slower hydration rate and smaller autogenous shrinkage.

From Fig. 7, a significant reduction of autogenous shrinkage is achieved in the internally cured samples. The total shrinkage is less than 20 $\mu\epsilon$ for both samples with 6% and 9% internal curing water at the age of 7 days. It is also noticeable from the figure that the internally cured samples stop shrinking at about 24 hours, and then shrinkage keeps constant (IC_6%) or the mortar expands slightly (IC_9%). Thus, it can be postulated that after 24 hours, the internal curing provided by the saturated cenospheres can fully compensate for the self-desiccation caused by cement hydration. If the amount of internal curing water is optimized, the elimination of autogenous shrinkage can be expected.

Fig. 7. Autogenous strain of control and internally cured cement mortars.

3.5. Compressive strength

Fig. 8 shows the compressive strength of mortars studied at the hydration age of 3, 7 and 28 days. As mentioned in Section 2.6, the samples were cured under sealed condition, and the compression tests were carried out on three samples at each age for each mix. The average of the three was reported in the figure with error bars representing the standard deviation among them. From the chart, the compressive strength of the mortars increased when the hydration age was increased, regardless whether the mortars have been internally cured or not. With the integration of 5% nonperforated cenospheres, the mortars have slightly lower compressive strength (3~5%) than the control one without any cenospheres. This strength reduction can be attributed to the lower compressive strength of the hollow cenospheres in the mortar samples. According to the manufacturer, 90% of the cenospheres used in current work can resist compression up to 22.06 MPa, which is lower than that of the mortar matrix. Hydraulic pressure method is used to measure the strength of cenospheres in which, cenospheres are loaded into a sealed container with water. Hydraulic pressure can then be applied to these cenospheres through a pump. The compressive strength of the cenospheres is determined based on the broken rates of cenospheres

at specific hydraulic pressure. Previous work [33] using cenospheres as lightweight fillers also shows that cenospheres can reduce the strength of concrete. With the comparison of the strength data between Control_0% and Control_9%, the strength discrepancy between the two is not seen to decrease as age increase. Thus it can be assumed that the pozzolanic reaction of cenospheres is not active or does not contribute significantly to the strength. From the figure, the internal curing effect can be found by comparing the strength between the control and internally cured mortars. At the hydration age of 3 days, the compressive strength of the internally cured mortars was lower than the control samples without any cenospheres. This could be caused by the lower strength of cenospheres. When the mortars were cured for 7 and 28 days, the strength of the internally cured samples caught up with the control ones, especially the one with 6% internal curing water. At these ages, the mortar with 6% internal curing water had the highest compressive strength. This can be caused by the promoted cement hydration with the extra water released from the saturated cenospheres. Being cured under sealed condition, the mortar matrix becomes short of moisture quickly with the fast cement hydration at early age, facilitating the release of water from the saturated cenospheres. The released water can prolong the fast cement hydration, leading to the faster strength development in the internally cured mortars. The promoted hydration was able to compensate the strength loss caused by the lower strength of cenospheres. The higher strength of internally cured sample was hardly achieved either by LWAs or SAPs [9,19,28]. For example, inclusion of 0.3% by mass of cement providing 3~4% internal curing water led to approximately 10% reduction in the compressive strength of HPC at 28 days [28]. Higher strength achieved by using cenospheres as internal curing agent can be attributed to their perfect spherical shapes, which can minimize stress concentration in concrete

induced by the voids of the internal curing agent. Thus the enhanced strength could be another great advantage by using cenospheres for internal curing.

Fig.8. Measured compressive strength for mortars under sealed condition.

3.6. Microstructure of cement mortar

The microstructure of mortars at the age of 28 days was also investigated. The samples were prepared as small fragment prized away from the failed cylindrical mortar specimens after compression test. The fragments were mounted on Al stubs with carbon tape, vacuum dried for 24 hours, Au sputter coated, and imaged in the high vacuum SEM mode. Evidence of cenosphere particles was found to be well distributed throughout the hardened mortar microstructure, as shown in Fig. 9. The dense microstructure of the mortar with w/c ratio of 0.35 can be clearly seen. From the figure, a number of cenospheres are found, in the form of either intact spheres or damaged particles. Fig. 10 shows the enlarged SEM images of intact cenosphere which were present in Fig. 9. The presence of intact cenospheres indicates the superior mechanical strength of cenospheres, which are able to withstand the shearing force from mechanical mixing. From Fig. 10, the intact cenospheres are surrounded by various hydration products. These products

could be precipitated from cement hydration and the possible reaction of cenospheres with calcium hydroxide. In addition, one may notice a post-loading crack around the cenospheres and the crack propagates into the adjacent microstructure. This indicates that compared to the strength of mortar matrix, the bonding between the cenospheres and adjacent microstructure is still lower. The bonding strength could be another factor that contributes to the lower strength of mortar incorporating nonperforated cenospheres as shown in Fig.8.

Fig.9. Microstructure of mortar with 6% internal curing water at the hydration age of 28 days.

Fig. 10. Intact cenospheres in the cement mortar with 6% internal curing water with hydration age of 28 days.

4. Conclusions

A chemical etching method is proposed in this study to produce perforated cenospheres so that they can be used as internal curing agent for HPC. Based on the experimental results of this work, the following conclusions can be drawn:

- (a) Water can be induced into cenospheres through acid etching. The porous structure of the cenosphere shell makes this etching process extremely efficient. The majority of pores created on the shell are smaller than 500 nm, with occasional pores in micron size ($< 2\mu\text{m}$).
- (b) The perforated cenospheres had water absorption as high as 180 wt.%. The loaded water can be readily released from the cenospheres in 24 hours under RH of 95%.
- (c) Internal curing provided by saturated cenospheres slightly retarded the setting of cement paste.
- (d) The internal curing was also found to lower the heat peak and shift the peak to the right. This indicates the slower hydration rate, corresponding well to the slower setting in the internally cured paste.
- (e) With internal curing, autogenous shrinkage of mortar was reduced significantly. The mortar stopped shrinking at around 24 hours, and it expanded slightly from 24 hours to 7 days. The mortars without internal curing had much higher autogenous shrinkage, and it shrank continuously with undergone hydration.
- (f) Perforated cenospheres used as an internal curing agent in cement mortar mixture resulted in slightly lower strength at early age, but with hydration progress, the compressive strength of internally cured mortar was higher than the ones without internal curing at the ages of 7 and 28 days.

In the future, internal curing by cenospheres will be optimized for HPC with various w/c ratios between 0.45 and 0.21, together with the incorporation of various supplementary cementitious materials. In addition, some fundamental knowledge of this new technique will be gained, including the role of fly ash particles in restrain the shrinkage of cement paste and the possible improvement on pozzolanic reactivity of cenospheres by chemical treatment and their effects on both the fresh and long-term durability of the cement-based materials.

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