Shrinkage of Internal Cured High Strength Engineered Cementitious Composite with Pre-wetted Sand-like Zeolite

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Abstract: In this paper, shrinkage and internal relative humidity of internal cured with calcinated zeolite particles of high strength engineered cementitious composite (HSECC) are experimentally investigated, in which the natural sand-like zeolite particles with average particle size of 0.18 mm were used as internal curing agent. Impacting factors, such as calcination, pre-wetting process and amount of internal curing agent, on shrinkage of HSECC were considered in the test program; meanwhile their effects on compressive strength of the composites were included as well. The test results show: 1) Two-stage progressing mode of shrinkage and internal relative humidity of HSECC are observed; 2) Applying the pre-wetted calcinated zeolite particles in HSECC, more than 60% of autogenous and/or drying shrinkage at 28 days is reduced while the strength of the composite remains as higher as the reference; 3) Calcination on zeolite particles is necessary for internal curing of high strength cementitious composites.

Key words: High-strength engineered cementitious composite; Autogenous and drying shrinkage; Internal curing; Zeolite particles

1. Introduction

To overcome the brittle nature of concrete, a class of high performance fiber

reinforced cementitious composite, called Engineered Cementitious Composites (ECC), has been developed in recent two decades [1]. This material has a unique property that after first cracking, tensile load-carrying capacity continues to grow, resulting in strain-hardening accompanied by multiple cracking. For each individual crack, the crack width first increases steadily up a certain level and then stabilizes at a constant value. Further increase in strain capacity is resulted from the formation of additional cracks until the cracking reaches a saturated state with crack spacing limited by the stress transfer capability of the fibers. After that, a single crack localizes and the load slowly drops with increased deformation. Typically, strain localization occurs at a tensile strain of 3-5%, with crack spacing of 3-6 mm and crack width around 60 μm [1]. However, in order to obtain this strain-hardening and multiple cracking performance, only a small amount of fine sand is allowed to be applied in order to control the fracture toughness of matrix [2-5]. Therefore, the shrinkage, including autogenous and drying shrinkages, must be higher than normal concrete due to its high cementitious materials content.

In addition, even the ability of crack width controlling of ECC is strong, a number of applications, such as permanent formwork for concrete structures, steel-concrete composite bridge decks and joint-less concrete pavements, still wish the material has a relatively higher strength, meanwhile remaining adequate ductility as long as satisfying the deformation requirements resulting from temperature change, shrinkage and mechanical loading [6, 7]. In these applications, cementitious composites with

properties of low moisture transport coefficient, high freezing resistance and low permeability are generally required apart from ductility. Strength is the governing parameter that controls the penetration of water and chemical agents during service of the structures at the stage without cracking. Strain capacity and formation of fine cracks are the critical points which control the long term durability of the structures at the stage that cracks may occur. Compressive strength of traditional ECCs is normally lower than 50 MPa, which apparently may not fully satisfy the requirements of above applications. High strength engineered cementitious composite (HSECC) is therefore needed to be developed. ECC with compressive strength around 80-100 MPa under normal curing condition had been developed recently [8]. However, the shrinkage of HSECC may be greater than normal strength ECC due to its very low water to binder ratio. The high shrinkage strain may result in cracking at an early age in structures that should shorten the service period without cracking. In addition, the large difference on shrinkage strain between ECC and normal concrete may lead to quick delamination of ECC-concrete composite structures.

Shrinkage of cementitious materials, including concrete, is one of the major sources of the formation of cracks in the structures. The magnitude of the shrinkage strain of cementitious materials is normally proportional to the amount of moisture loss [9-12]. In general, environmental drying and cement hydration are the two major processes leading moisture loss inside the material. As environmental humidity is lower than the humidity inside of the material, the water inside of material evaporates and shrinkage

arises, which is called drying shrinkage. Another process causing moisture loss is through cement hydration, which is called self-desiccation and the corresponding shrinkage of the material is called autogenous shrinkage. Generally, the autogenous shrinkage of cementitious materials is a function of water to cement ratio of the material. The higher the water to cement ratio, the lower the autogenous shrinkage. Strength of cementitious material is inversely proportional to water to cement ratio. Therefore, high strength cementitious material normally has higher autogenous shrinkage comparing with that of normal strength one.

To reduce the shrinkage of cementitious materials, it is necessary to complement or slow down the moisture loss. Use of pre-wetted lightweight aggregate as an internal reservoir to provide water as the concrete dries is an effective method to decrease autogenous shrinkage of high strength concrete [13-15]. However, the particle size of lightweight aggregate is generally larger than 4 mm, which is too large to be used in ECC as the larger particle will weaken the fiber bridging stress that controls strain hardening and multiple cracking performance of the material. Another method to reduce shrinkage of concrete is to use super absorbent polymer, but the addition of super absorbent polymer in concrete will decrease concrete strength due to the introduction of additional pores in cement matrix [16, 17]. Therefore, it is necessary to seek materials that may be used for internal curing of HSECC, meanwhile satisfying the requirements on fiber bridging of ECC materials. In this paper, zeolite particles with size of 0.18 mm were used as internal curing agent of HSECC.

Shrinkage and internal relative humidity of HSECC with pre-wetted sand-like zeolite addition are measured. The test results show that by applying calcined zeolite particles in HSECC, internal relative humidity can significantly be increased under both sealing and drying condition. Meanwhile, autogenous and drying shrinkage of the composite are greatly reduced. Efficiency on shrinkage reduction of HSECC may achieve 60% while strength remains as higher as the reference.

2. Experimental Program

Details of Materials and Specimens

The purpose of this test program goes to regulate shrinkage of HSECC. An optimized cementitious binder composition of 70% cement, 10% silica fume, 10% grounded granulated blast furnace slag, 10% fly ash in weight, which achieving the highest compressive and bending strength of matrix under given water to binder ratio and normal curing condition [18], was used in the present experiments. Calcium sulfoaluminate cement (SAC), that possesses extra high early-age strength [19], was used as cementing material. The chemical compositions of SAC and silica fume, grounded granulated blast furnace slag and fly ash, used in the tests are showed in Table 1. Silica sand with particle size of 0.075 to 0.150 mm was used to form the mortar matrix. Constant water to binding material ratio (w/b) of 0.2 and constant sand to binder ratio of 0.833 were used in the matrix mixture proportion. Polyvinyl alcohol fiber (PVA) supplied by Kuraray Company in Japan was employed as reinforcement and the fiber properties are given in Table 2. Constant fiber content of 2% in volume

fraction is utilized in the composites.

Based on the above reference mixture or called ordinary curing mixture (OC), six internal cured mixtures (IC) were designed using sand-like zeolite particles as internal water reservoir, which replaces silica sand in the proportions. The average particle size of the zeolite is 0.18 mm that was produced in China. Zeolite is aluminosilicate mineral containing relatively large amount of micropores and physically bonded water in it. To investigate the effect of calcination on the efficiency of the shrinkage reduction of the composites, two kinds of zeolite particles were prepared. One was the particles undergo 500⁰C calcination in a muffle furnace for 30 minutes, called Zeolite-500. Another was the natural particles without calcining, called Zeolite-N. Therefore, we designed two internal cured mixtures, IC-1Y and IC-2Y using Zeolite-N and Zeolite-500 respectively as internal curing agent. Label Y means the zeolite particles were pre-wetted in water for 3 days before mixing with other components. To study the effect of pre-wetting of the zeolite particles on shrinkage of the composite, two internal cured mixtures were designed, IC-2Y and IC-2N, where N indicates the zeolite particles without pre-wetting were utilized. To investigate the effect of the amount of internal agent on shrinkage of the composite, two zeolite particle additions of 15% and 20% of the silica sand in weight were used respectively in the tests, forming internal cured mixtures of IC-2Y and IC-3Y. It should be noted that the total water content, including water absorbed by zeolite, was keeping constant in above internal cured mixtures. Therefore constant water to binder ratio of 0.20 in above mixtures was presented.

However, it is understandable that the internal curing water should stay in the pores of the internal curing agent. Therefore, the above water should not influence the formation of capillary pores of the cement matrix theoretically, which may be reflected through strength tests. To investigate the effect of the pre-absorbed water on shrinkage and strength properties of the composite, two additional internal cured mixtures, named as IC-4Y and IC-5Y were designed, which assuming about 0.26 gram of water per gram of zeolite that was determined from nitrogen adsorption test, was pre-absorbed before mixing with cement and other components, and therefore this absorbed water was not included in the mixing water. Thus, a little higher water to binder ratio in IC-4Y and IC-5Y is displayed compared with other mixtures. A polycarboxylate superplasticizer with 30% solid content was used to guarantee all the fresh mixtures have a similar flow-ability. All the mix proportions used in the present study are listed in Table 3. Fig.1 shows the particle distribution of the Zeolite-N and Zeolite-500. For comparison, the size distribution of the quartz sand used in the present study is displayed also. Clearly, calcination has a little effect on particle size of the zeolite (particles between 1 to 20 μm increase a little and particles between 200 to 1000 μm decrease a little) and a similar most probable particle size of 0.15-0.2mm among the three particles is observed. The specific surface area of Zeolite-500, Zeolite-N and quartz sand is 49 m^2/g , 41 m^2/g and 1.2 m^2/g respectively. The pore size distribution of the Zeolite-500 and Zeolite-N and quartz sand is displayed in Fig.2 based on nitrogen adsorption test. As expected, high pore volume is obtained in Zeolite-500 than that of Zeolite-N. Heating the zeolite particles will evaporate the physically bonded water originally contained in the zeolite

and allow more pores become empty. Certainly, pore volume in Zeolite-N is still higher than that of quartz sand. The pore content of Zeolite-500, Zeolite-N and quartz sand is 0.26 ml/g, 0.045 ml/g and 0.002 ml/g respectively according the nitrogen adsorption test.

The mold used to cast the specimens for shrinkage measurement was made of plexiglass with inner dimensions of 100×100×400 mm. Two plexiglass plates with dimensions of 20×100×400 mm were used as recoverable filler respectively along the two long inside sides of the mode. Therefore, the actual size of the specimen is 60×100×400 mm. Before casting, the four inner sides of the mold were covered with four pieces of removable plastic sheets with 2 mm thickness and the bottom of the mold was covered with a thin vinyl sheet with 1 mm thickness to reduce the frictional resistance between the mold and the concrete. After the initial set of the concrete, the inner four removable plastic sheets were lifted to create the “free restraint” conditions of the shrinkage test. Meanwhile, the two filler plates along the two long sides were removed also to create space for specimen drying.

Devices for Measuring the Relative Humidity, Temperature and Deformation

In this study, the humidity and temperature at the center of the test specimen were measured. Resistance based digital sensor that can measure humidity and temperature at the same time was used. The measuring accuracies of relative humidity and temperature are 2% and 0.5 °C, respectively. The measuring method of internal relative humidity is the same as used in [20]. To maintain the sensor at the designated

location in the specimen, a PVC tube with an inner diameter of 15 mm was used to hold the sensor. One end of the PVC tube was covered with a plastic sheet glued to the end. To maintain the moisture exchange with the surrounding matrix, two rectangular holes were made at the surface of the PVC tube. In order to prevent fresh cement paste from flowing into the tube through the rectangular holes, a steel bar with a little smaller diameter than that of the PVC tube was placed into the tube first during material casting. A few minutes after casting, the steel bar was removed from the tube and the sensor was inserted. To ensure the measured humidity and temperature reflect the real values inside the material, two rubber O-shaped rings with a 2 mm thickness were used to isolate the free gap between the PVC tube and the sensor bar. The O-shaped ring was just above the sensory section of the sensor. In the meantime, at the top of the tube, the gap was sealed by an industry sealant to guarantee that the moisture did not leak through the gap. Thus, the sensory section is only connected to the material at the point where we wish to measure its humidity and temperature values. The deformation was measured by two linear variable differential transducers (LVDTs) mounted on the two long ends of the specimen as used in [20]. The measuring range of the LVDT is 2 mm and the measuring accuracy is 1 μm . To ensure the LVDTs were in good contact with the specimen, two small cylinder bars were pre-cast into the material at the centers of the two long ends of the specimen. The sensory bar of the LVDT was direct contact with the small bar during testing.

Material Mixing, Specimen Casting and Curing Procedures

The mixing procedure of the composite material consists of the following steps. (1) Matrix preparation: The matrix was prepared in a concrete mixer. First, the cementitious material and silica sand were mixed together for 2 minutes at low speed. Then water with superplasticizer and pre-mixed zeolite-water slurry, if pre-wetted zeolite was used, were gradually added, and mixing was continued for 2 minutes which result in a uniform fluid matrix. Within this period, the bottom of the mixing bowl should be scraped manually to ensure that no solid materials stick to the bottom. After such scraping, the matrix was mixed at a higher speed for 1 minute before the addition of fibers. (2) Addition of fibers: the fibers were gradually spread into the mixer by hand as the matrix was mixed at a slow speed. The fibers must be added slowly to ensure homogeneous distribution with no fibers bundled together. Before casting, plastic sheets used to seal the specimen were put into the mold first. In the mean time, the two copper measuring probes were fixed at the designated locations. Then, the fresh composite was cast into the mold in two layers and was consolidated by a vibrating table. After compacting, the PVC tube with the steel bar inserted was put into the concrete at the appointed depth from the casting surface. While placing the tube, the vibration was started again to make sure the PVC tube was in effective contact with the surrounding concrete. After finishing the surfaces, the casting face was also covered with a plastic sheet to prevent moisture exchange with its surroundings. About 2 hours after casting, the steel bar was removed from the tube and it was verified that there was no liquid water left inside the tube before the humidity sensor was inserted. Meanwhile, after the initial set of the concrete (about 2 hours from casting), the four removable thin

221 sheets were slowly lifted and a 2 mm gap between the specimen and the mold was
222 created. Afterward, two LVDTs were installed at the two long ends of the specimen.
223 Fig.3 shows the overall schematic diagram of the humidity and deformation
224 measurement set-up. During the test, the humidity and temperature were automatically
225 recorded every 10 min by a personal computer. In order to investigate the shrinkage
226 behavior under both sealing and drying conditions, two identical specimens with the
227 same mixture proportion were cast for each concrete. After 3 days of concrete casting,
228 the plastic film covering the five surfaces of the one of the two specimens was removed.
229 While the other specimen maintains the sealing state to compare with the drying
230 specimen. Fig.4 is a photo showing the two parallel specimens under testing. The tests
231 were continued until 28 days since material casting. All tests were performed in a
232 laboratory under room temperature. Beside shrinkage tests, 100×100×100 cube
233 specimens were cast also and cured in the laboratory under plastic film sealing for
234 determining compressive strength of the composites.

235
236 After the tests, the humidity sensors were calibrated using saturated salt solution
237 under constant temperature of 22⁰C. The saturated salt solution was prepared with
238 distilled water and analytically pure salts. The sensory section of the sensor and
239 saturated salt solution were placed in a sealed container made of the corrosion
240 resistant and non-hydrophilic material. For each calibration process, the final
241 displayed relative humidity that does not change with time was used as the measured
242 value of the sensor under the specific moisture environment. Each sensor was

calibrated at five different humidity levels, and then its calibrating curve is obtained.

The calibration curves are displayed in Fig.5. Based on the calibrating results, the measured humidity data was revised.

3. Experimental Results and Discussion

Compressive Strength of Internal Cured HSECC

The compressive strength measured by cube specimens with the dimension of 100mm×100mm×100mm of seven mixtures of HSECC at 28 days are listed in Table 4. First, as the silica sand is replaced with pre-wetted zeolite particles in the weight of 15%, whether the zeolite is suffered from calcination or not, the compressive strength of the composite is increased. The increasing rate of the mixture with calcinated zeolite is higher than that with no-calcinated zeolite. This positive effect of zeolite addition on compressive strength of the composite may be due to the pre-adsorbed water by the zeolite particles leading the decrease of actual volume of capillary pores of cement paste. Certainly, on the other hand, the negative effect of relative-weak porous zeolite particles on the strength may not exceed the above positive action in the case of 15% replacement. Second, comparing the compressive strength of mixtures of IC-2Y and IC-2N, obvious lower strength of IC-2N is obtained than that of IC-2Y. The only difference between them is that if the zeolite particles are pre-wetted or not. Clearly, as zeolite particles are not pre-wetted, the addition of them will decrease the composite strength of the composite. The reduction on strength may be because the addition of un-wetted zeolite particles will adsorb mixing water and

release gas that contains in its micro-pores. The released gas will create additional pores in the matrix, which in turn decrease the strength of the composite. In addition, calcination can enhance the ability of gas releasing of zeolite. Therefore, the calcinated zeolite may be used for manufacturing lightweight or air-entrained concrete. Third, as the replacement of silica sand with pre-wetted zeolite particles achieving 20% in weight, the strength of the composite starts to decrease (see the strength of IC-2Y and IC-3Y), even though the strength reduction is only 2.7% comparing to that of the reference (OC). An optimized addition of pre-wetted zeolite particles in cementitious matrix is existed in the view of material strength. Fourth, excluding the adsorbed water by zeolite particles from the total mixing water will lead to decrease of composite strength (see strength values of IC-2Y and IC-4Y; IC-3Y and IC-5Y). This is because the above positive effect on strength is eliminated and the negative effect is left only. The strength reduction may depend on the amount of water excluding in the mixture. Based on present test results, as 0.26 gram of water per gram of Zeolite-500 was assumed, the excluding of mixing water resulted strength reduction is about 4-6% (85.64 and 80.57 MPa; 79.83 and 76.67 MPa respectively for 15% and 20% sand weight replacement). However, such excluding on water adsorbed by zeolite particles from the total mixing water may obviously reduce the shrinkage of the composite. The improvement on shrinkage performance may be more important than the resulted strength reduction of 4-6%. This can be found in the next section.

Development of Shrinkage, Internal humidity and Temperature of Internal Cured

HSECC

From shrinkage test, the development of deformation along the long direction of the specimen and internal relative humidity and temperature at the center of the sample can be recorded. Afterward, the complete shrinkage strain versus age diagram since composite set can then be obtained. Here, the setting point of the composite is determined according to the deformation characteristic before and after setting, i.e. the end of the initial swelling of the specimen is defined as the setting point of the composite [20]. Fig.6 to 12 presents the shrinkage-age, internal relative humidity-age and temperature-age diagrams since specimen casting of all the seven mixtures under sealing and drying conditions respectively. From the test results, we can observe that the progress of internal relative humidity of HSECC since specimen cast follows two-stage mode that had been found in concrete already [20-22]: a water-vapor saturated stage with 100% relative humidity (stage I) followed by a stage the relative humidity is gradually decreasing (stage II). The shrinkage-age diagram follows a two-stage mode also: First develops at a fast speed within the first day after casting and then goes into a slow growing stage afterwards. The shrinkage strain connecting first and second stages may be called ε_1 for later analysis. In overall, the development of shrinkage and internal relative humidity of HSECC under both sealing and drying conditions are greatly influenced by the addition of the zeolite particles. Impacting factors may include the status of the zeolite particles (calcinated or un-calcinated), mixing method (pre-wetting or not) and adding amount. The shrinkage strain and relative humidity at 28 days after casting under sealing and drying conditions, as well

as the shrinkage value of ε_1 , defined in the above description, of all the seven mixtures are summarized in Table 3.

First, let us look at the test results of the reference mixture, OC, displayed in Fig.6a and 6b. As already observed in concrete [20, 21], the progress of internal relative humidity of HSECC since specimen cast presents a water-vapor saturated stage with 100% relative humidity (stage I) followed by a stage the relative humidity gradually decreasing (stage II) mode. The reduction of internal relative humidity in early-age HSECC due to cement hydration is extremely obvious. Certainly, surface drying will further decrease the internal relative humidity. However, the difference on relative humidity between sealing and drying samples is relatively small due to the very low water to binder ratio and relatively higher water consumption of cement hydration. The amount of water left for diffusion is less. The relative humidity at the center of the test sample of HSECC at 28 days after casting is 59.7% and 52.9% respectively under sealing and drying condition, which is even lower than that of 100 MPa concrete [23]. **Meanwhile, large shrinkage strain is developed within the first day after casting ($\varepsilon_1=1263 \mu\text{m/m}$) even that the internal relative humidity still remains at 100% in this period.** After this period, the shrinkage is further growing at a relatively slow speed. At 28 days after casting, the shrinkage strain is $1370 \mu\text{m/m}$ and $1481 \mu\text{m/m}$ respectively under sealing and drying states. Clearly, more than 90% of the shrinkage strain at 28 days are developed within the first days after casting. This may be considered as an important shrinkage characteristic of the present

HSECC with calcium sulfoaluminate cement. In addition, it is interesting to note there is a small expansion of the sample around 3 days after casting that should be due to the temperature rise of the specimen, where the peaks of temperature and expansion coordinate each other well, see Fig.6b. This phenomenon was also observed by Turcry et al. in studying autogenous shrinkage and thermal deformation of cement paste at early-age [24].

As pre-wetted no-calcinated zeolite particles (Zeolite-N) were used to replace 15% silica sand in weight in the composite, mixture IC-1Y (see Fig.7), the moisture status inside of the composite was improved compared to the reference mixture (OC). The temperature peak occurs early comparing with the reference mixture. The internal relative humidity at 28 days becomes 81.2% and 57.7% respectively under sealing and drying conditions. Accordingly, shrinkage strain at 28 days decreases to 917 $\mu\text{m/m}$ and 1018 $\mu\text{m/m}$ respectively under sealing and drying states. **The value of ε_1 becomes 853 $\mu\text{m/m}$. More than 30% shrinkage reduction comparing with the reference is observed.** As the same amount of pre-wetted calcinated zeolite particles (Zeolite-500) was used, mixture IC-2Y (Fig.8), the shrinkage and internal relative humidity of the composite are further decreased and increased respectively. The internal relative humidity at 28 days after casting becomes 85.5% and 70.3% respectively under sealing and drying conditions. Accordingly, shrinkage at 28 days further decreases to 804 $\mu\text{m/m}$ and 896 $\mu\text{m/m}$ respectively under sealing and drying states. ε_1 becomes 711 $\mu\text{m/m}$. More than 44% shrinkage reduction comparing to the

reference is obtained. Obviously, efficiency on shrinkage reduction of Zeolite-500 is higher than that Zeolite-N, that means calcination on zeolite can help to increase the capacity of water storage in the pores. However, the test results on IC-1Y are interesting as well because the results indicate that the natural zeolite particles can also be used as internal curing agent of cementitious materials for shrinkage reduction. Certainly, calcination on zeolite particles further improved the function of a water reservoir in the matrix. In addition, it is valuable to note the addition of zeolite particles in the composite does not reduce strength of the composite as the replacement ratio is 15%. This should be a specific advantage to using zeolite particles as internal curing agent of cementitious materials. As state previously, to investigate the effect of pre-wetting or not of the zeolite particles on shrinkage reduction of the composite, two internal cured mixtures are designed, named IC-2Y and IC-2N, where N indicates the zeolite particles without pre-wetting were utilized. In the test Zeolite-500 was used as internal curing agent. Now, let us to analyse the test results. From Fig.8 and Fig.9, we may clearly observe the zeolite particles without suffering pre-wetting process almost do not have the expected function of shrinkage reduction. Meanwhile, because the calcinated zeolite particles will absorb free water and release external gas during hardening, the strength of the composite will be decreased. Therefore, it is a necessary process of pre-wetting the zeolite particles in order to reduce shrinkage of the materials.

As 20% of the silica sand is replaced with pre-wetted calcinated zeolite particles

(Zeolite-500), i.e. mixture IC-3Y (Fig.10), the shrinkage strain at 28 days is further decreasing becomes 730 $\mu\text{m/m}$ and 868 $\mu\text{m/m}$ respectively under sealing and drying states. ε_1 becomes 604 $\mu\text{m/m}$. More than 51% shrinkage reduction comparing to the reference is observed. Meanwhile, the internal relative humidity of the composite at 28 days continues to increase, becomes 85.5% and 71.4% respectively under sealing and drying conditions. In addition, as the addition of the zeolite particles up to 20%, the negative effect of porous particles on strength of the composite becomes relatively obvious, for instance the compressive strength at 28 days of IC-2Y and IC-3Y is 85.64 MPa and 79.83 MPa. Certainly, we do have some additional methods to enhance the frame of solid particles, which in turn can compensate the strength reduction. However, by contrast, we have a few technical ways to reduce shrinkage of low water to binder ratio cementitious matrix at present.

In principle, internal curing water should stay in the pores of the internal curing agent. The water contained in the pores should not influence the formation of capillary pores of the cement matrix. Therefore, as water content is kept constant, the addition of pre-wetted zeolite particles will decrease free water content that will influence the capillary structure of the cement matrix. Water to binder ratio of all above internal cured mixtures (IC-1Y, IC-2Y and IC-3Y) is constant of 0.2. **In the case of the water contained in the zeolite pores is excluded, how will this influence the shrinkage and internal relative humidity of the composite?** Therefore we design mixtures, IC-4Y and IC-5Y (Fig.11 and Fig.12), in which 0.26 gram of water per gram of Zeolite-500 that

was used. From Fig.11 and 12, we can clearly see even less shrinkage strain and even higher internal relative humidity are obtained. For the same amount of the zeolite particle addition, for instance, IC-2Y, IC-4Y (15%) and IC-3Y, IC-5Y (20%), the shrinkage strain at 28 days under drying is 896 $\mu\text{m}/\text{m}$, 726 $\mu\text{m}/\text{m}$ and 868 $\mu\text{m}/\text{m}$, 618 $\mu\text{m}/\text{m}$. Reduction rate on shrinkage is 54% and 63% respectively for IC-4Y and IC-5Y comparing to the reference. Certainly, in this case, the negative effect of porous zeolite particles on strength of the composite becomes more obvious and the corresponding compressive strength at 28 days of IC-4Y and IC-5Y becomes 80.57 MPa and 76.67 MPa. Comparing with the efficiency of shrinkage reduction, the decrease of strength is acceptable, 1.8% and 6.5% reduction comparing to the reference mixture (OC). **In addition, the cost to produce the calcinated zeolite particles is lower than the cost of cement. Therefore in the view of cost of ECC, the change due to the use of calcinated zeolite should be very small.**

4. Conclusions

Shrinkage and internal relative humidity of internal cured with calcinated zeolite particle high strength engineered cementitious composite (HSECC) are experimentally investigated in this paper. The natural zeolite particles with size of 0.18 mm were used as internal curing agent. The possible influencing factors, including calcination, pre-wetting process and amount of internal curing agent, on shrinkage reduction of HSECC are considered in the tests. Meanwhile, their effects on compressive strength of the composites are investigated as well. The following

conclusions can be drawn from the present study:

- The development of internal relative humidity of HSECC since casting exhibits first a vapor saturated stage ($RH=1$, stage I), followed by gradually reducing stage ($RH<1$, stage II). Meanwhile, two-stage mode of the progress of shrinkage strain with age starting from composite setting is observed, behaving as a fast developing stage within a few hours followed by an increasing stage with a gradually reduced rate. The shrinkage developed in the first stage is normally developed within the humidity saturated stage.
- Applying the pre-wetted calcined zeolite particles in HSECC, more than 60% of autogenous and/or drying shrinkage at 28 days is reduced while the strength of the composite remains as higher as the reference;
- Calcinations and pre-wetting are necessary processing steps for internal curing of cementitious composites with zeolite particles. Use of the zeolite particles without calcination will decrease the efficiency of shrinkage reduction by 30%. Use of un-wetted calcined zeolite particles in HSECC may reduce the strength of HSECC.

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Table 1. Chemical composition of the cementitious materials used in tests (wt%)

No	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	SO ₃	LOI
SAC	6.19	42.9	24.16	1.04	1.96	0.48	0.08	12.91	8.91
Silica fume (SF)	90.56	0.81	0.41	0.52	0.95	1.59	0.63	-	3.72
Fly ash (FA)	47.02	5.08	35.06	3.88	1.36	1.30	1.18	0.89	1.85
Slag (SG)	38.83	38.70	12.92	1.46	4.63	0.37	0.28	0.60	0.06

Table 2. Properties of PVA fibers

Types	Density (g/cm ³)	Tensile strength (MPa)	Elastic modulus (GPa)	Diameter (mm)	Length (mm)
PVA fiber	1.2	1620	42.8	0.039	12

Table 3. Mix Proportions of test series

No	Cementitious Materials Total(Cement:SF:SG:FA)	Sand	Zeolite-N	Zeolite-500	Water	PVA fiber (volume,%)	Plasticizer (%)
OC	1(0.70:0.10:0.10:0.10)	0.833	0	0	0.20	2	0.88
IC-1Y	1(0.70:0.10:0.10:0.10)	0.708	0.125	0	0.20	2	0.89
IC-2Y	1(0.70:0.10:0.10:0.10)	0.708	0	0.125	0.20	2	0.88
IC-2N	1(0.70:0.10:0.10:0.10)	0.708	0	0.125	0.20	2	0.94
IC-3Y	1(0.70:0.10:0.10:0.10)	0.666	0	0.167	0.20	2	0.90
IC-4Y	1(0.70:0.10:0.10:0.10)	0.708	0	0.125	0.23	2	0.86
IC-5Y	1(0.70:0.10:0.10:0.10)	0.666	0	0.167	0.24	2	0.83

Table 4. Properties of internal cured HSECCs

No	Compressive strength at 28 days (MPa)	Shrinkage of ϵ_1 ($\mu\text{m}/\text{m}$)	Shrinkage at 28 days, Seal ($\mu\text{m}/\text{m}$)	Shrinkage at 28 days, Dry ($\mu\text{m}/\text{m}$)	RH at 28 days, Seal (%)	RH at 28 days, Dry (%)
OC	82.04	1263	1370	1481	59.7	52.9
IC-1Y	83.03	853	917	1018	81.2	57.7

IC-2Y	85.64	711	804	896	85.5	70.3
IC-2N	75.80	1021	1115	1363	72.0	53.4
IC-3Y	79.83	604	730	868	85.5	71.4
IC-4Y	80.57	588	679	726	85.0	71.6
IC-5Y	76.67	467	509	618	90.3	75.8

520

521 Table and Figure Captions

522 Table 1. Chemical composition of the cementitious materials used in tests (wt%)

523 Table 2. Properties of PVA and steel fibers

524 Table 3. Mix Proportions of test series

525 Table 4. Properties of internal cured HSECCs

526 Fig.1 Particle size distribution of Zeolite-500, Zeolite-N and quart sand

527 Fig.2 Pore distribution of Zeolite-500, Zeolite-N and quart sand based on nitrogen
528 adsorption

529 Fig.3 Schematic diagram of internal relative humidity and deformation measurement

530 Fig.4 Experimental set-up for humidity and deformation measurement of HSECC
531 under plastic sealing and drying conditions

532 Fig.5 Calibrating curves of RH sensors

533 Fig.6 Development of shrinkage and internal relative humidity (a) and temperature (b)
534 with age of OC mixture

535 Fig.7 Development of shrinkage and internal relative humidity (a) and temperature (b)
536 with age of IC-1Y mixture

537 Fig.8 Development of shrinkage and internal relative humidity (a) and temperature (b)
538 with age of IC-2Y mixture

539 Fig.9 Development of shrinkage and internal relative humidity (a) and temperature (b)
540 with age of IC-2N mixture

541 Fig.10 Development of shrinkage and internal relative humidity (a) and temperature
542 (b) with age of IC-3Y mixture

543 Fig.11 Development of shrinkage and internal relative humidity (a) and temperature
544 (b) with age of IC-4Y mixture

545 Fig.12 Development of shrinkage and internal relative humidity (a) and temperature

546 (b) with age of IC-5Y mixture

Figure

Fig.1 Particle size distribution of Zeolite-500, Zeolite-N and quart sand

Fig.2 Pore distribution of Zeolite-500, Zeolite-N and quart sand based on nitrogen adsorption

Fig.3 Schematic diagram of internal relative humidity and deformation measurement

Fig. 4 Experimental set-up for humidity and deformation measurement of HSECC at early age under plastic sealing and drying conditions

Fig.5 Calibrating curves of RH sensors

(a)

(b)

Fig. 6 Development of shrinkage and internal relative humidity (a) and temperature (b) with age of OC mixture

(a)

(b)

Fig.7 Development of shrinkage and internal relative humidity (a) and temperature (b) with age of IC-1Y mixture

(a)

(b)

Fig.8 Development of shrinkage and internal relative humidity (a) and temperature (b) with age of IC-2Y mixture

(a)

(b)

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(a)

(b)

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(a)

(b)

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(a)

(b)

Fig.12 Development of shrinkage and internal relative humidity (a) and temperature (b) with age of IC-5Y mixture