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Influences of superabsorbent polymers on the strength and shrinkage properties of low water-to-binder ratio expansive concrete

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Low water-to-binder ratio (W/B) is the main method to obtain the excellent mechanical properties of high performance concrete, which is also the main factor causing its shrinkage. Expansive agent is often used to reduce or even eliminate shrinkage. But the expansion effect isn't obvious in the middle and later stage because of water shortage. Internal curing has been considered to be a very effective way to maintain the relative humidity of the interior. This paper studied the influence of SAP and additional water diversion on the strength and the limit expansion ratio of the expansive concrete with low W/ B. SAP could reduce the shrinkage of 0.62 µm/m ~1.91 µm/m, and the compressive strength was further influenced. In microscopic analysis, SAP was confirmed to promote the hydration degree of cement and expansive agent, especially in the middle and later stages of hydration; the hydration products and the expansion products AFt intergrowth, the structure was more compact. Considering the influence of SAP on its expansion and mechanical properties, the reasonable amount of SAP was recommended as 0.2 %, and the reasonable water flow was 10~20 times.

Key words: Superabsorbent polymers, Expensive concrete, Low water-to-binder ratio, Compressive strength, Limit expansion ratio, Microanalysis.

Introduction

The low water-to-binder (W/B) ratio is an important feature of common high-performance concrete, while it also remains as the main factor causing material shrinkage and structure cracking [1, 2]. In order to prevent the generation of shrinkage cracks in concrete structures, the expansive concrete (EC) with the incorporation of different types of expansive agents (EA) (such as calcium sulfoaluminate, magnesium oxide and calcium oxide) is widely used in engineering practices. The EA that generate volume expansion in the hardening process of concrete counteract to some extent the shrinkage deformation, and thus improve efficiently the crack resistance of material. In the early years, the EA are generally adopted in the concrete with high W/B ratios, which can hydrate adequately to produce sufficient expansion in the good curing condition. However, with the increasing application of high-performance concrete with low W/B ratios, the effects of EA are limited largely due to that the water within the concrete is not enough to accomplish adequately the hydration process, especially in the midlate stage, thus weakening the expansion and crack

resistance effects of concrete. The basic approach for solving the insufficient hydration problem of EC is to increase the interior humidity of concrete [3, 4].

At present, most of the projects in China use external maintenance for concrete, and it is mainly divided into traditional methods and modern chemical maintenance methods. It is difficult to form effective curing of concrete interior by traditional methods such as watering and damp cloth [5, 6]. They will increase the difficulty of maintenance construction of some complicated structure such as the side and top surface of the buildings. And traditional methods also waste a lot of manpower and water resources. The chemical maintenance methods mainly use a paraffin-based high-concentration water emulsion and a latex-type emulsion to form a waterrepellent layer on the concrete surface to prevent moisture loss. These products are characterized by high dispersion, non-toxicity, and high curing efficiency. But they are expensive and the market application is limited. Low W/B concrete has lower permeability due to its lower water gel, and it is difficult for external water to diffuse into the interior of concrete. Therefore, external curing can't effectively alleviate its shrinkage. To address this problem, Philleo (1991) [7] pioneered the concept of internal curing (IC), which was firstly defined in the American Concrete Institute (ACI) guide of 308R-2001 as supplying water throughout a freshly placed cementitious mixture via pre-wetted lightweight aggregates that release water as needed for hydration

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[8]. Then, lots of researches have been carried out, mainly focusing on different types of internal curing materials, their microcosmic mechanisms as well as their influences on the physical and mechanical properties of cement-based materials [7, 9-12], and the results also shows the validity of IC in the humidity maintenance of concrete [9]. In the aspect of internal curing materials, the superabsorbent polymers (SAP) with a wide application has been verified to be effective in reducing or even eliminating the plastic shrinkage [13], the autogenous shrinkage [8, 14-16] and the drying shrinkage [17] of concrete. However, the SAP has an unfavorable effect on concrete strength due to that a certain amount of pores are generated in the concrete after the SAP releases the absorbed water [18, 19], although it might enhance the freeze-thawing resistance capability of concrete [4, 20]. On the other side, the additional water (AW) amount is an important factor affecting the curing effect of concrete with SAP. An appropriate amount of AW help improve the hydration of cementitious materials and the physical and mechanical properties of concrete. Nowadays, with the increase of researches and applications, the performance and IC mechanism of SAP have been studied extensively [21]. For mechanical properties, SAP was often found to have a negative effect on the strength of concrete at early ages [22, 23], whereas a higher strength at later ages was reported [24]. For shrinkage, it was suggested that SAP could reduce the plastic shrinkage [25], autogenous shrinkage [26] and drying shrinkage [17]. For durability, some studies showed that the introduction of SAP had almost no negative effect on the permeability [27, 28], although a certain amount of pores were left in the hardened concrete by SAP.

To date, most studies focus respectively on the effects of EA or SAP on the properties of concrete, while the combined effects of EA and SAP have received less attention, especially on the high-performance EC with low W/B ratios. This study investigates experimentally the effects of SAP on the strength and restrained expansion of EC with a low W/B ratio, considering the variation of mixing amounts of SAP and AW amounts, and performs a microanalysis based on the technologies of X-ray diffraction (XRD) and scanning electron microscope (SEM) to analyze the microstructure and the corresponding IC mechanism of concrete. According to the main results of this study, some suggestions are also proposed for further studies and engineering applications.

Experimental Materials and Methods

Materials selection

The experimental study concentrates on the influences of SAP on the properties of EC and the related microcosmic mechanism, and the selection of experimental

Table 1. Chemical and mineral compositions of the cement.

Main oxides and related proportions (%)											
SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	SO ₃						
20.62	20.62 6.13		58.73	6.16	3.8						
Mineral compositions and related proportions (%)											
C_3S	C_2S	C ₃ A	C ₄ AF	CaSO ₄	Other						
55.88	19.48	9.17	9.77	3.85	1.85						

materials is a key issue to control the accuracy of experimental results. The EC is a mixture of the cement, the coarse aggregate, the fine aggregate, the expansive agent, the internal curing agent (SAP), the admixtures and a certain amount of water.

In this study, the ordinary Portland cement with the strength grade of P.O 42.5 according with the China National Standards GB175-2007 was used. Table 1 shows the main chemical and mineral compositions of the cement. The density of cement is 3.08 g/cm^3 , and the residue rate through an 80 µm sieve is 1.5 %.

The coarse aggregate of concrete utilized in this study is the continuous grading gravel with a particle diameter range of 5~25 mm. The apparent density and stacking density of the gravel are 2.78 g/cm³ and 1.55 g/cm³ respectively, and the related crush value is 7.1 %, and silt content is 0.6 %. The selected river sand is used as fine aggregate, with a fineness modulus of 2.8, an apparent density of 2.65 g/cm³, a stacking density of 1.549 g/cm³, a porosity of 35 %, and a mud content of 2.5 %.

The calcium sulphoaluminate-calcium oxide expansive agents for concrete (CA) is adopted. Besides, three main types of admixtures, including the polycarboxylate superplasticizer (PS) with a solid content of 40 % and a specific gravity of 1.06, the defoamer with a solid content of 20 % and a specific gravity of 1.03, and the sodium gluconate (SG) with a solid content of 99 % which is used as set retarder, are used.

In this experiment, the SAP is obtained by crosslinking copolymerization from suspended acrylic and acrylamide. The particle size distribution of SAP is $10~30 \mu m$, with a water absorption rate in distilled water of 300 g/g, and 25 g/g in cement slurry with w/b of 0.3.

Material mixing ratio

The research object of this paper is the EC with the w/b ratio of 0.28. The cement and CA are considered as cementitious materials (CM), all with 10 % CA addition by mass of CM. During the experiment, the mixing amount of SAP and the amount of AW intake are changed to investigate their effects on the concrete compressive strength and the limit expansion rate, while the amounts of other concrete components keep constant. Referring to the determination method of water absorption rate and additional water amount for the SAP in cement slurry. Jensen et al. [17] proposed the values for AW that are necessary to secure complete

Cases	EC-0	EC-10SAP-1	EC-20SAP-1	EC-30SAP-1	EC-10SAP-2	2 EC-20SAP-2	EC-30SAP-2	2 EC-10SAP-3	BEC-20SAP-3	EC-30SAP-3
cement	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
CA	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
sand	1.27	1.27	1.27	1.27	1.27	1.27	1.27	1.27	1.27	1.27
gravel	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
water	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
SAP	0	0.001	0.001	0.001	0.002	0.002	0.002	0.003	0.003	0.003
AW	0	0.01	0.02	0.03	0.02	0.04	0.06	0.03	0.06	0.09
SG	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004
PS	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005

Table 2. The mixing ratio design of experiment referenced to CM mass.

hydration of cement by calculating the chemical shrinkage: w/c (water-cement ratio) ≤ 0.36 , the addition of AW = 0.18 w/c. However, in high-performance concrete with low W/B, the hydration degree of cementitious materials is relatively low, the chemical shrinkage force of the system should be less than the value calculated by the above method, and the additional water diversion amount used to offset the chemical shrinkage of cementitious materials is also less. When taking the addition of AW into consideration, it is necessary to consider the dosage, type, particle size and mixing method of SAP since they have important influence on IC effects. Therefore, reasonable mixing amount of SAP and AW in concrete has not formed a consensus.

For all the above reasons, the mixing amount of SAP in this study is determined to be 0.1 %, 0.2 % and 0.3 % respectively (the cases corresponding to three different mixing amounts are denoted by SAP-1, SAP-2 and SAP-3, respectively). The AW intake amounts are respectively 10 times, 20 times and 30 times of the SAP amount, which are correspondingly denoted by 10SAP, 20SAP and 30SAP.

The mixing ratio design of this experiment is shown in Table 2, in which the data denote the proportions relative to the masses of CM.

Experimental method

In order to improve the distribution uniformity of SAP particles in the concrete during the mixing process, the SAP and EA were first mixed and stirred sufficiently, and then put into a single horizontal-axis mixer together with other dry materials for a prestirring lasting for 3 minutes. In the next step, 90 % of water including the mixing and additional intake water was added into the mixer for stirring of 1.5 minutes, and finally, the rest all water and admixtures were added for a sufficient stirring of 3 minutes.

The compressive strengths of concrete cured for 3, 7 and 28 days respectively were tested according to the Standard Test Method for Mechanical Properties of Ordinary Concrete in China (GB/T 50081-2002).

The restrained expansion rates of concrete cured for 1, 3, 7, 14, 28 and 42 days were tested on the basis of

the method stated in the Technical Specifications for Application of Concrete Admixtures in China (GB50119-2013).The size of concrete specimen is $100 \times 100 \times$ 300 mm (Length × Width × Hight). After casting, the specimens were cured under standard conditions: first, the specimen surface was covered by using a wet cotton (or plastic) cloth to prevent effectively the evaporation of water; then the hardened specimen was put into water with a constant temperature of $20 \pm 2 \text{ °C}$ for 14 days; then, the specimen was moved to the standard indoor environment with a constant temperature of $20 \pm 2 \text{ °C}$ and a humidity of $60 \pm 5 \%$ for 28 days. Fig. 1 shows the test specification for the concrete limit expansion ratio and the specification of the longitudinal limiter.

In this study, the X-ray diffraction analyzer manufactured in Japan with a produce model of DMAX-2500PC was utilized to measure the change of characteristic diffraction peak values of hydration products in different ages, and to investigate the influence of SAP on the hydration products at different ages. Besides, the Japan-made low-vacuum electron microscopy scanner (JSM-6380LA) was adopted to take photos of specimen appearance with the magnification of 2000 and 5000, which helped to observe comprehensively the cross sections of specimens. Fig. 2. shows the photos of X-ray diffractometer with a produce model of DMAX-2500PC and JSM-6380LA scanning electron microscopy.

Experimental Results and Analyses

Generally, the incorporation of SAP and additional water has an important influence on the performance of concrete. In this experiment, the compressive strength and the restrained expansion ratio of EC are selected as the key parameters to analyze the influences of SAP and AW, aiming to determine a best mixing amount of SAP and additional water.

Compressive strength

Fig. 3 shows the compressive strengths of concrete specimens with the same amount of SAP but different times of AW. When SAP dosage is 0.1 % of the quality



Fig. 1. The test specification for the concrete limit expansion ratio and the specification of the longitudinal limiter.

of CM, the reduction range of concrete strength is 1.4~11.3 % compared with the blank group when the W/B increases by 1 % (denoted by EC-10SAP-1). This is mainly due to SAP's early water absorption which leads to the reduction of W/B in the system at the age of 7d ago, more unhydrated cement particles appeared. But its later water release promoted the hydration of CM, which has little impact on 28d strength; when the W/B increased by 2 % (denoted by EC-10SAP-2), the range of strength of concrete increases from 9 % to 15 % compared with the blank group. It shows that the excess water in the early stage of the system and the water released by SAP in the later stage promote the hydration of cementitious materials after ensuring that SAP is saturated in water absorption, which is conducive to the growth of strength. When the W/B increased by 3 % (denoted by EC-10SAP-3), compared with the blank group, the 3d strength of concrete decreases by 3.0 %, while 7d and 28d strength increase by 6.9 %



(a) X-ray diffractometer



(b) Scanning electron microscopy



and 4.7 %, respectively.

As shown in Fig. 3b, when SAP dosage is 0.2% of the quality of CM, the change law of concrete strength is basically similar to SAP-1 in Fig. 3a when the W/B increases by 2 % (denoted by EC-20SAP-1); when the W/B increased by 4 % (denoted by EC-20SAP-2), the strength of concrete at each age is at its maximum, which is nearly close to the blank group; when the W/B increased by 6 % (denoted by EC-30SAP-2), the reduction range of concrete strength reaches 7.5~15.9 % compared with the blank group, this mainly because the excessive water diversion leads to a sharp decrease in the water cement ratio, resulting in a decrease in strength.

As shown in Fig. 3c, when SAP dosage is 0.3 % of the quality of CM, the strength of 3d and 7d decreases by 15.3 % and 15.0 % respectively compared with that of blank group. But the strength of 28d increases by 3 % when the W/B increases by 3 % (denoted by EC-10SAP-3), which indicates that the strength growth caused by the hydration of CM by SAP in the later stage makes up for the strength reduction caused by the increase of W/B in the earlier stage; When the W/B



Fig. 3. Compressive strengths of concrete specimens with the same amount of SAP but different times of AW. The average and the standard deviation of 3 specimens are shown for each mixture and age.

increased by 6 % (denoted by EC-20SAP-3) and 9 % (denoted by EC-30SAP-3), the maximum reduction of concrete strength compared with the blank group is 34.5 %, which is caused by the sharp decrease of W/B caused by excessive water diversion, resulting in the reduction of strength.

Fig. 4 shows the compressive strengths of concrete



Fig. 4. Compressive strengths of concrete specimens with the same times of AW but different SAP amount. The average and the standard deviation of 3 specimens are shown for each mixture and age.

specimens with different amounts of AW relative to SAP. Fig. 4a exhibits the specimen strengths corresponding to the AW amount of 10 times of the quality of SAP (denoted by EC-10SAP), while the amount of SAP ranges from 1 ‰ to 3 ‰ (denoted by EC-10SAP-1, EC-10SAP-2 and EC-10SAP-3). The strength of concrete at 3d and 7d shows a law of decreasing, and

then the strength develops rapidly. The strength of 28d shows little difference compared with the blank group, the largest drop of concrete strength at 3d and 7d is 15.3 % and 15.0 %, respectively, and the fluctuation range of strength at 28d is $-1.4 \sim 3.0$ %.

Fig. 4b shows the specimen strength variation when the AW amount is 20 times of the quality of SAP (denoted by EC-20SAP). It can be found that the compressive strength generally presents a decreasing tendency as the SAP incorporation amount increases from 1 % to 3 %. When the SAP amount is 1 %, the specimen strength exceeds that of EC-0 case by about 9.0~15.4 %, indicating that the SAP incorporation at this amount help improve the concrete strength to a significant extent. As the SAP amount increases to 2 % (EC-20SAP-2), the specimen strength decreases to the level close to that of EC-0, and a further increasing in SAP amount (like 3 % denoted by EC-20SAP-3) cause a continuous decrease in concrete strength (then lower than the case of EC-0 by 7.0~22.5 %).

The specimen strength variation is similar to Fig. 4b when the AW amount is 30 times of the quality of SAP (denoted by EC-30SAP) shown in Fig. 4c. However, the intensity of all ages decreases significantly compared with the blank group, the largest decreases of 3 d, 7d and 28d are 35.1 %, 21.8 % and 16.3 %, respectively.

Through the analysis of the above test results, it is found that: compared with the blank group, the mixing of SAP and AW reduces the strength of EC at 3 days except 20SAP-1 and 7 days except 20SAP-1 and 30SAP-1. It also improves 28d strength when the SAP and AW are 20SAP-1, 30SAP-1, 20SAP-2 and 10SAP-3. Due to the large amount of CM and low W/B (< 0.36) of concrete, there will be a certain amount of unhydrated cement particles [29]. The water used for the hydration of cement continues to decrease with the hydrating of cement, which will lead to the reducing of the humidity of the paste. SAP can make up for the decrease in humidity and reduce the difference of humidity in different areas by releasing internal water, in addition, the time when relative humidity began to fall is significantly delayed [30, 31]. SAP's water absorption and the additional water reduce the early hydration of cementing materials [32], which will lead to the reduction of earth strength. However, when the internal humidity of concrete is reduced to a certain extent, the water absorbed in SAP will be released to promote the continuous hydration of the cement particles, which is conducive to the later strength development of concrete. The swelling SAP decreases in volume after water loss, leaving a certain amount of large pores in the hardened body, which will be hazardous to the development of strength. Moreover, some AW can promote hydration, but the excessive water will inevitably lead to a sharp drop in W/B, resulting in a decrease in strength [33].

SAP pores and unreasonable estimation of AW

diversion are also important factors in the strength. Therefore, it is necessary to determine the appropriate amount of SAP and water diversion, promote the hydration of cementitious materials. The key to solve this problem is making its strength enhancement effect higher than SAP hole weakening effect.

Limit expansion ratio

Fig. 5 shows the limit expansion ratio of concrete specimens with the same amount of SAP but different



Fig. 5. Limit expansion ratio of concrete specimens with the same amount of SAP but different times of AW.

times of AW. It can be seen from the figure that compared with the blank group, the addition of SAP and AW makes the limited expansion rate curve become more gentle after the peak, indicating that the volume change of concrete gradually decreases. Moreover, the difference of expansion and contraction deformation decreases, which improves the crack resistance of concrete.

As shown in Fig. 5a, the increase of W/B from 0.29 to 0.31 has no significant effect on limit expansion rate in the early stage when SAP dosage is 0.1 % of the quality of CM, but the shrinkage of concrete is observably reduced in the later stage. The limited expansion rate of 42d is as much as that of the blank group (EC-0), the maximum reduction of the 42d limited expansion rate is 117 ppm compared to the blank group (EC-0).

As shown in Fig. 5b, when SAP dosage is 0.2 % of the quality of CM and the amount of water diverted is 10 times and 20 times of SAP, the time for concrete to start shrinkage is extended by 17-22 days compared with the blank group, and the limited expansion rate of 42d is reduced by 191 ppm at the maximum. When the amount of water diverted is 30 times, the increase of W/B in the early stage increases the contraction. However, the hydration of cement and expansion components promote by the slow water release in the later stage of SAP compensates for the contraction caused by the increase of W/B.

As indicated by Fig. 5c, when SAP dosage is 0.3 % of the quality of CM and the amount of water diverted is 10 times and 20 times of SAP, the time for concrete to start shrinkage is extended by 9-12 days compared with the blank group, and the limited expansion rate of 42d is reduced by 188 ppm at the maximum. When the amount of water diverted is 30 times, SAP is less effective in making up for the shrinkage caused by the increase in W/B.

Fig. 6 shows the limit expansion ratio of concrete specimens with the same times of AW but different SAP amount. Fig. 6a gives the specimen limit expansion ratio corresponding to the additional water amount of 10 times of the quality of SAP (denoted by EC-10SAP), while the amount of SAP ranges from 1 ‰ to 3 ‰ (denoted by EC-10SAP-1, EC-10SAP-2 and EC-10SAP-3). The samples are increased by the SAP dosage of 1 ‰ and the W/B of 1 %. The improvement effect of concrete limit expansion rate is first enhanced and then weakened, but it is better than the blank group. When the SAP content is 2 ‰, the improvement effect is the most obvious, the age at which the concrete began to shrink is delayed by 22 days, and the limited expansion rate of 42d reduces by as much as 191 ppm compared with EC-0.

The specimen limit expansion ratio variation is similar to Fig. 6a when the additional water amount is 20 times of the quality of SAP (denoted by EC-20SAP)



Fig. 6. Limit expansion ratio of concrete specimens with the same times of AW but different SAP amount.

shown in Fig. 6b. The improvement effect is the most obvious when SAP dosage is 2 ‰, but the age of concrete begins to shrink is delayed for 17 days, and the limited expansion rate of 42d reduces by a maximum of 186 ppm compared with EC-0. As shown in Fig. 6c, when the AW amount is 30 times the mass of SAP, SAP is not conducive to the expansion of concrete in the early stage, although the shrinkage of concrete is significantly reduced in the later stage, with a maximum reduction of 114 ppm compared with the blank group.

The addition of SAP and AW promotes the hydration of cement and expansion components, improves the expansion and shrinkage properties of concrete. The limited expansion rate of 42d was 62-191 ppm lower than that of the blank group. When the SAP content is 0.2 % and the water diversion is 10 times and 20 times, the improvement effect of concrete limit expansion rate is the best. Taking into account the influence of SAP and AW on the strength of EC and the development of limited expansion rate, the reasonable mixing amount of SAP is 0.2 % when EC can get the best internal curing, and the reasonable parameter range of water diversion is 10-20 times.

For the convenience of observation, the micro test takes the paste composed of cement and expansion agent as the research object. It removes sand and gravel that do not participate in the hydration reaction, and the amount of other components remains unchanged except SAP and AW. Taking the samples without SAP and AW as the blank group (CU), and with the SAP dosage of 2 ‰ and the AW dosage of 1.5 % of the mass of CM as the comparison group (SCU). The effect mechanism of SAP on the properties of EC is obtained through the comparative analysis of XRD and SEM test results of the two samples. The samples are all maintained in a way that limited the expansion rate.

XRD

The skin of each hydrated sample is removed after the specified curing time, and the internal sample is knocked into small pieces of 0.2-0.3 mm, and then immersion in anhydrous ethanol to terminate the hydration of CM. The specimens are ground down to 10 microns by using a three-headed agate grinder and then tested by XRD. The hydration process of each sample is analyzed by detecting the change of the characteristic diffraction peak of the hydration products of 3d and 28d. XRD analysis of the crystalline hydration products includes calcium hydroxide (CH), ettringite (AFt), carbonated calcium carbonate and unhydrated β -silicate dicalcium (β -C₂S).

The XRD graph curves of the characteristic diffraction peak value and peak intensity of two samples are shown in Fig. 7 at the age of 3d and 28d respectively. As shown in Fig. 7a, CH characteristic peak is more obvious through 3d hydration which indicates that the hydration rate of each sample is fast. The two groups in hydration of beta C_2S and the area of characteristic peak surrounded by AFt are similar. However, the CH characteristic peaks formed by SCU cover slightly more area than CU group, manifesting that SAP and AW with a bit of extra promote the hydration of CM, but the effect is not obvious.

As shown in Fig. 7b, the production of CH and AFt increases significantly, and the amount of β -C₂S without



Fig. 7. XRD maps of 3d and 28d.

hydration decreases observably during the curing period from 3d to 28d. And the area of the characteristic peaks of CH and AFt formed by SCU is notably more than that of CU group, indicating that SAP remarkably promotes the hydration of cement particles and EA, and leads to generate more expansion products and hydration products.

SEM

Select 5~8 mm long rod sample in the middle and break it from the middle position after breaking the sample, exposing the fresh section of uncarbonized calculi body, so as to observe the microstructure of the sample section more clearly and comprehensively. In order to study the effect of SAP incorporation on the hydration of cementitious materials, this test selects the position inside and the boundary of the hole so as to observe the formation state of AFt in the sample, and takes a 2000 to 5000 fold magnification photo of the morphology of the two samples at the age of 3d and 28d.

Fig. 8 shows the SEM images at different ages of CU and SCU. As shown in Fig. 8a, a large number of AFt can be observed clearly in large holes and other areas at the age of 3d, and the morphology of AFt is rodshaped, flowered and clustered. The growth state of AFt in the hole and other parts of the hardened cement with SAP (SCU) is more vigorous than the blank group (CU), which can prove that SAP and AW promote the generation of AFt. AFt is the main expansion factor that causes the microexpansion of concrete, which partly explains why SAP can improve the limit



(a) 3d age SEM



(b) 28d age SEM

Fig. 8. SEM images at 3d and 7d of CU and SCU.

expansion ratio of concrete.

As shown in Fig. 8b, as the curing age of the sample reaches 28d, a large amount of AFt has been formed in the sample, which intersects with calcium silicate hydrate. Moreover, the growth of AFt in SCU samples is more vigorous than CU, the expansion effect of EC is better developed. AFt is filled between the small cracks in the sample, which makes the structure more compact. From the data of 28d compressive strength (Fig. 3b), the improvement of compactness can offset the strength loss caused by SAP hole.

With the continuous hydration of cement and expansion components, the internal capillary water loss of concrete leads to the decrease of relative humidity. Driven by the humidity difference and capillary tensile stress, SAP releases water to compensate for the decrease in humidity and improves the humidity distribution, reducing the humidity difference between different regions. In the process of hydration, AFt needs to combine and adsorb a large amount of water molecules. The swollen SAP particles form an effective moisture network within the concrete that continues to provide moisture for the formation of AFt, especially inside the pores and at the pore boundaries. Therefore, the AFt in SCU is more vigorous than in CU.

Conclusion

This paper mainly studies the influence of the incorporation of internal curing agent SAP and AW on the strength of low W/B EC and the limit expansion rate, and further explains the influencing mechanism by using XRD and SEM for micro-analysis. The main conclusions are as follows:

(1) The mixing of SAP and AW reduces the strength of most of the EC at 3d and 7d, but the later strength of concrete can be significantly improved when the

content is reasonable.

(2) The addition of SAP and AW significantly reduces the shrinkage of EC by 0.62-191 ppm compared with the blank group.

(3) Considering the influence of SAP and AW on the strength of EC and limit expansion rate comprehensively, the strength and deformation performance of EC can be significantly improved when the SAP content is 0.2 % of the quality of CM and the AW amount is 10-20 times of SAP quality.

(4) Through microscopic analysis, the mixing of SAP and AW has little effect on the hydration of EC at 3d, but it remarkably promotes the hydration of 28d, resulting in a significant increase in the formation amount of CH and AFt. In the later stage, SAP slowly releases the water absorbed in the earlier stage, improving the hydration degree of CM and the content of AFt. In addition, the right amount of pores left by SAP after water release will not affect the strength of concrete negatively, but improve the limit expansion rate and the durability of concrete.

References

- V. Mechtcherine, M. Gorges, C. Schroefl, A. Assmann, W. Brameshuber, A.B. Ribeiro, S. Zhutovsky, Mater. Struct. 47 (2014) 541-562.
- M. AN, J. ZHU, W. ZUO, J. Build. Mater. 4[2] (2001) 159-166.
- H.-G. QIN, M.-R. GAO, C.-M. PANG, SUN Wei. J. Build. Mater. 14 (2011) 394-399.
- 4. S. Mönnig. Otto-Graf J. 16 (2005) 193-202.
- J. Liu, C. Shi, X. Ma, K.H. Khayat, J. Zhang, D. Wang, Constr. Build. Mater. 146 (2017) 702-712.
- 6. M. Wyrzykowski, P. Lura, F. Pesavento, D. Gawin, J. Mater. Civ. Eng. 24 (2012) 1006-1016.
- 7. R.E. Philleo, Mater. Sci. Concr. II (1991) 1-8.
- 8. ACI 308R, in "Guide to Curing Concrete" (American Concrete Institute, 2001) p.2.
- 9. P. Lura, in "Autogenous Deformation and Internal Curing of Concrete" (Delft University of Technology, 2003) p.11.
- 10. O.M. Jensen, P.F. Hansen, Cem. Concr. Res. 31[4] (2001) 647-654.
- M. Wyrzykowski, S. Ghourchian, S. Sinthupinyo, N. Chitvoranund, T. Chintana, P. Lura, Cem. Concr. Compos. 71 (2016) 1-9.
- F. Liu, J. Wang, X. Qian, J. Hollingsworth, Cem. Concr. Res. 95 (2017) 39-46.
- L. Dudziak, V. Mechtcherine, in Proceedings of the 2nd International Conference of Textile Reinforced Concrete (ICTRC), September 2010, edited by W. Brameshuber (RILEM Publications SARL Press, 2010) p. 129.
- V. Mechtcherine, M. Gorges, C. Schroefl, A. Assmann, W. Brameshuber, A.B. Ribeiro, D. Cusson, J. Custódio, E.F. Da Silva, K. Ichimiya, Mater. Struct. 47 (2014) 541-562.
- 15. O.M. Jensen, P.F. Hansen, Cem. Concr. Res. 32 (2002) 973-978.
- D. Snoeck, O.M. Jensen, N. De Belie, Cem. Concr. Res. 74 (2015) 59-67.
- 17. S. Mönnig, H.W. Reinhardt, in Proceedings of the RILEM Conference on Volume Changes of Hardening Concrete:

Testing and Mitigation, August 2006, edited by O.M. Jensen, P. Lura, K. Kovler (RILEM Publications SARL Press, 2006) p. 67.

- M.T. Hasholt, M.H.S. Jespersen and O.M. Jensen, in Proceedings of the International RILEM Conference on Use of Superabsorbent Polymers and Other New Additives in Concrete, August 2010, edited by O.M. Jensen, M.T. Hasholt and S. Laustsen (RILEM Publications SARL Press, 2010) p. 117.
- 19. P. Lura, F. Durand, A. Loukili, K. Kovler, O.M. Jensen, in Proceedings of the RILEM Conference on Volume Changes of Hardening Concrete: Testing and Mitigation, August 2006, edited by O.M. Jensen, P. Lura, K. Kovler (RILEM Publications SARL Press, 2006) p. 117.
- 20. M.T. Hasholt, O.M. Jensen, S. Laustsen, Adv. Civ. Eng. Mater. 4 (2015) 237-256.
- V. Mechtcherine, H.-W. Reinhardt, in "Application of Superabsorbent Polymers (SAP) in Concrete Construction" (Springer Press, 2012) p. 1.
- 22. B. Craeye, G. De Schutter, in Proceedings of the RILEM Conference on Volume Changes of Hardening Concrete: Testing and Mitigation, August 2006, edited by O.M. Jensen, P. Lura, K. Kovler (RILEM Publications SARL Press, 2006) p. 909.
- 23. B. Craeye, M. Geirnaert, G.D. Schutter, Constr. Build. Mater. 25[1] (2011) 1-13.
- 24. D.P. Bentz, M. Geiker, O.M. Jensen, in Proceedings of the

International Seminar on Self-Desiccation and Its Importance in Concrete Technology, June 2002, edited by B. Persson, G. Fagerlund (Lund University Press, 2002) p. 195.

- 25. L. Dudziak, V. Mechtcherine, in Proceedings of the 2nd International Conference of Textile Reinforced Concrete (ICTRC), September 2010, edited by W. Brameshuber (RILEM Publications SARL Press, 2010) p. 129.
- 26. F. Wang, Y. Zhou, B. Peng, Z. Liu, S. Hu. ACI Mater. J. 106 (2009) 123-127.
- 27. H.W. Reinhardt, A. Assmann. Proc. BMC 9, Warsaw. (2009) 291-300.
- V. Mechtcherine, in: H.W. Reinhardt (Ed.), RILEM State of the Art Reports, 2, Springer (2012) 115-134.
- 29. Powers, T.C., Brownyard, T.L., Research Laboratories, PCA. Bulletin. 22 (1948). 473-488.
- Xiang-ming Kong, Zhen-lin Zhang, Zi-chen Lu. Mater Struct. 48[9] (2015) 2741-2758.
- N. Nestle, A. Kühn, K. Friedemann et al. Micropor Mesopor Mater. 125 (2009) 51-57.
- 32. Janis Justs, Mateusz Wyrzykowski, Frank Winnefeld et al. J Therm Anal Calorim. 115 (2014) 425-432.
- 33. Marianne Tange Hasholt, Ole Mejlhede Jensen, Konstantin Kovler et al. Constr Build Mater, 31 (2012) 226-230.
- Hong-gen Qin, Mei-rong Gao, Chao-ming Bang et al. J Build Mater (in Chinese). 13[4] (2011) 394-399.