Absorption and desorption behaviors of superabsorbent polymers and their effects on volume changes in cement-based materials

学　位　論　文　要　旨

Dissertation Abstract

Absorption and desorption behaviors of superabsorbent polymers and their effects on volume changes in cement-based materials

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提出年月：　2017 年 9 月 25 日

Abstract

Superabsorbent polymer (SAP) has evolved as a multifunctional admixture to mitigate autogenous shrinkage in high performance concrete (HPC). It is essential to estimate SAP characters to disclose fundamental properties towards application in cement-based construction materials. In this study, autogenous deformation of cement-based materials are investigated with an emphasis on absorption and desorption behaviors of SAP. It is suggested that the tea bag method is prone to be affected by agglomeration of SAP particles. The graduate cylinder method is considered as a useful way to evaluate absorption capacity of SAP in cement environment. Furthermore, internal water released from SAP contributes to the early age expansion. Differences in the expansion are related to the distribution of water released from SAP. Gelation of a part of mixing water with SAP can be used as an effective way to mitigate autogenous shrinkage without adding extra water. It is concluded from these results that autogensous deformation, in particular the early age expansion, is significantly influenced by the absorption and desorption behaviors of SAP.

1. Introduction

With the advent of high performance concretes (HPC), early age shrinkage cracking in concrete has been of great interest. Early age cracking, which is primarily due to restrained autogenous shrinkage, may affect the durability of the concrete. In the early age before setting when the cement paste is still fluid, autogenous shrinkage is equivalent to chemical shrinkage. It results from the fact that the volume of hydration product is smaller than these of the reactants, i.e. cement and water. When all the cement grains are in contact with water and the hydrates percolate in cementitious systems, the measurable chemical shrinkage diminished. Then autogenous shrinkage becomes dominant in early age cement systems. In the hardened stage, autogenous shrinkage occurs due to self-desiccation while a rigid skeleton is formed to resist volume changes.

Some methods to reduce autogenous shrinkage have been proposed. Internal curing has been well known for its effectiveness to mitigate autogenous shrinkage. Lightweight aggregate and superabsorbent polymers (SAP) have been used as internal curing materials. In particular, SAP is a interesting material since it has various functions with respect to water control. SAP is a group of cross-linked polyelectrolyte which starts swell upon contact with aqueous fluids resulting in the formation of a hydrogel. SAP has the ability to absorb a significant amount water from the surrounding and to retain water within their structure without dissolving. SAP can increase their volume immediately as soon as they contact with water, reaching saturation with a few minutes. The main drying force of absorption behavior of SAP is osmotic pressure which is dependent on the ionic nature of the aqueous fluids. At the late period of hydration, the absorbed water by SAP will be released gradually to the surrounding cement matrix, and voids created by SAP collapse will remain. The main driving force for the desorption of SAP is the osmotic pressure and the gradient in relative humidity. This absorption and desorption behavior of SAP is a key aspect in the SAP technology in terms of their practical applications to cement-based materials. However, its process has not been fully understood. Therefore, in this study, autogenous deformation of cement-based materials are investigated with an emphasis on absorption and desorption behaviors of SAP.

2. SAP used in this study

Seven types of SAP (A, B, C, D, 1, 2 and 3) are used for cement paste or mortars, respectively. SAP-A, B, C and D are produced by aqueous polymerization while SAP-1, 2 and 3 are obtained by inverse suspension polymerization. SAP-A, B ,C and D are irregular shape, while SAP-1, 2 and 3 are almost mono-sized spherical powders (Fig.1). Tiny particles of SAP-2 and SAP-3 are gathered around large particles due to a surfactant. SAP-A, SAP-1 and SAP-2 are sieved to obtain two particle size ranges, large (300~600μm) and small (150~300μm). SAP-B and C are also sieved to obtain two particle size ranges, large (200~500μm) and small (<200μm). SAP-B, C, D and 3 of the original grading are also used.

3. Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementious materials

3.1. Kinetics of water absorption and desorption of SAP measured by the tea bag method and the graduated cylinder method

Fig.2 shows changes in absorption capacity of SAPs in a simulated pore solution. Similar tendency of absorption capacities of SAP in cementitious systems could be obtained either by the tea bag method and by the graduated cylinder method. However, when SAPs are used for the purpose of water control on rheology modification, various situations in terms of

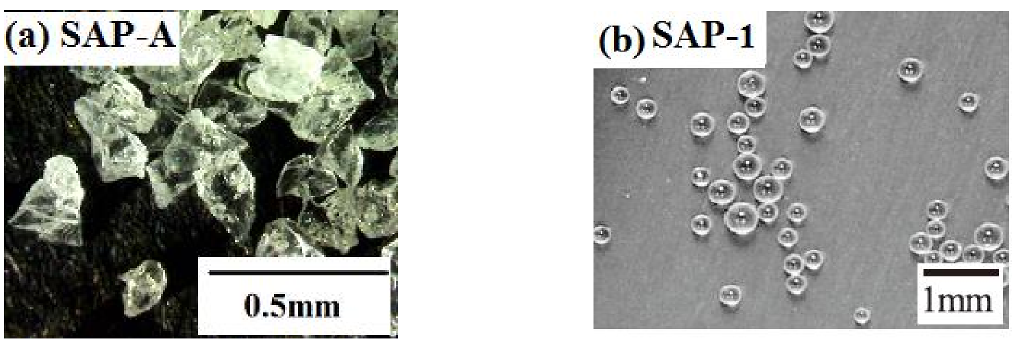
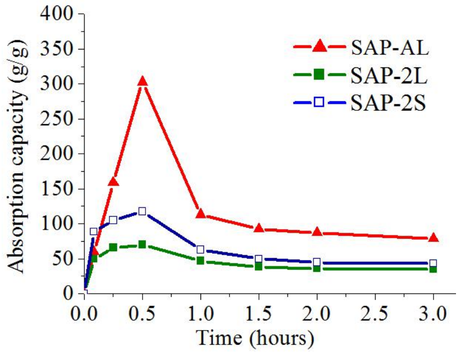
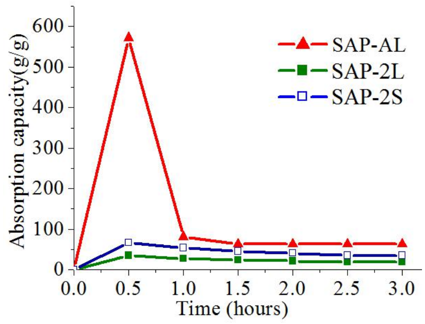


Fig.1 SAP-A and SAP-1 at dry state



(a) Absorption capacity evaluated by the tea bag method



(b) Absorption capacity evaluated by the graduated cylinder method

Fig.2 Change in absorption capacity with time evaluated in simulated pore solution

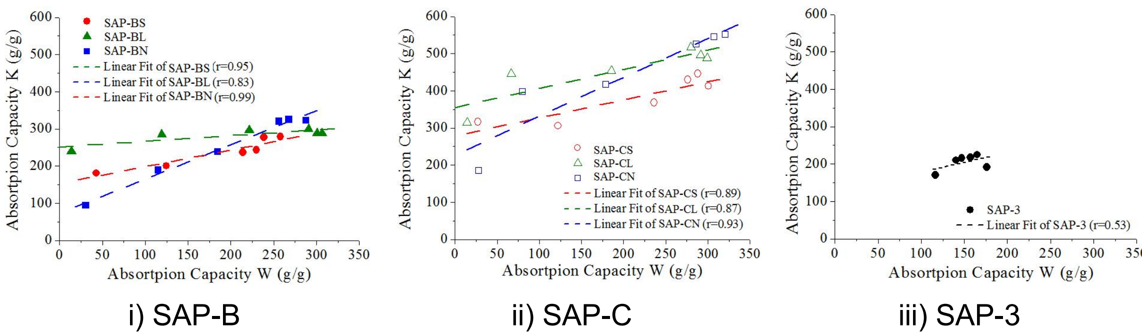
alkaline environment are expected in practical application. Further investigation is necessary to establish a proper measurement technique to evaluate swelling and absorption capacity of SAP in cement environment. However, at least the graduated cylinder method gives the consistent results with those of the tea bag method. Furthermore, effects of gravity draining are excluded in the testing conditions. Therefore, the graduated cylinder method can be used as a simple way to evaluate absorption and desorption capacity of SAP under more similar conditions to real concrete.

3.2. Comparison of absorption capacity of SAP measured by the modified tea bag method and the filtration method

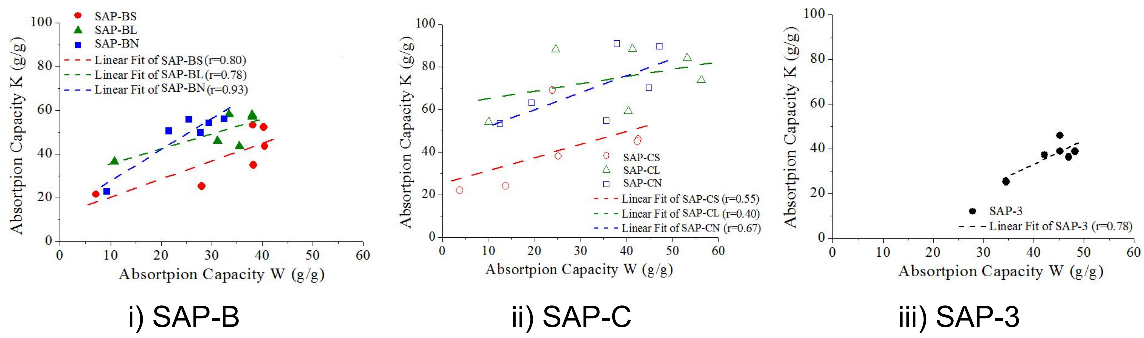
The comparison between the results of absorption capacities is discussed from the viewpoint of retention of interparticle liquid on SAP particles during the test period.

Fig.3 shows the relationship between absorption capacities measured by the modified tea bag method and the filtration method. At the same time, the absorption capacity K measured by the filtration method is always appreciably greater than the absorption capacity W. SAP particles are easy to form agglomeration on the corner of a tea bag, which caused an obviously reduction in the contacting area of SAP particles and test fluid. In practice, insufficient swollen SAP is observed in the tea bag. The insufficient swollen SAP may affect the smaller value of absorption capacity obtained by the tea bag method.

In addition, the increase in absorption capacity W for the testing period (ΔW) is obviously greater than that in absorption capacity K (ΔK) for SAP-BS and SAP-BL, while ΔW and ΔK were very close for SAP-BN. The similar trend is also observed in SAP-C. The SAP that is not sieved showed a stable increase in absorption capacity than others. For SAP-3, the rate of increase in absorption capacity W to that in K is almost the same as SAP-BS and SAP-BL. Surfaces between SAP particles become larger with swelling. The larger particles, the more capillary water. The water between small particles is less since the packing of small



(a) De-ionized water



(b) Filtered cement slurry (w/c=4.3)

Fig.3 Correlation of absorption capacities measured the two methods

SAP is denser than that of large SAP. The dense packing makes a narrow channel to reduce capillary water. The water held by capillary forces between SAP particles cannot be totally removed by the modified tea bag method, while almost excess water dropped off in the filtration method. Therefore, these tendencies may results in a large increase in absorption capacity during the test period measured by the modified tea bag method. In short, the increase in absorption capacity W during the test period seems to be contributed by the retention of interparticle liquid. Furthermore, for each SAP, the time-dependent change of absorption capacity shows a similar variation tendency whether SAP is immersed into de-ionized water or cement slurry filtrate. Thus, the tests with de-ionized water may be used for simple comparison of absorption capacity in cement environment while the absolute absorption capacity is quite different between the water and the cement slurry filtrate.

3.3. Effect of SAP on plastic viscosity of cement pastes at early age

Fig.4 shows time-dependent changes in plastic viscosity of the cement pasts. Dosage of SAP is determined to absorb 10% of mixing water. The development of the plastic viscosity corresponds to the sorption kinetics observed in the tea bag method and the graduated cylinder method. Increase in plastic viscosity may result from the decrease in freely available water in cementitious system and may mean the increase in internal friction of material. These changes in the plastic viscosity are recorded before the initial setting time when the

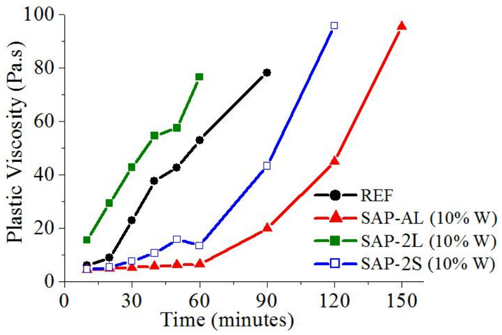


Fig.4 Development of plastic viscosity in cement paste at early age (W/C=0.28)

water of SAP has released already. The water released from SAP would supply the freely available water as a lubricant to alleviate internal friction and postpone the growth of plastic viscosity. Here, all the specimens with SAP have the same amount of 10% of mixing water within SAP. Relatively large desorption of water from SAP-AL at early age would prevent the quantity of freely available water from diminishing quickly, leading to the slowest growth in plastic viscosity. On the other hand, although SAP-2S absorbs almost the same amount of water as SAP-2L during mixing process, the value of plastic viscosity is almost close to the reference at the first measuring of time. It may be related to the density of SAP particles and the moisture distributions in cementitious system. Since the particle sizes of SAP are different, the numbers of SAP particles are different among the cement pastes. Therefore, their spatial distribution, in other words, the number densities of internal water reservoirs are different among the specimens at the beginning. In addition when the internal water is released, the initial distributions of moisture are also different among the specimens. This could affect the initial evolution of internal friction.

4. Early age autogenous deformation of mortars with low water to cement ratio

Fig.5 shows autogenous deformation after the initial setting time (i.e. Deformation is adjusted to zero at the time of initial setting). Fig.6 shows measurements of bleeding rates of mortars. A polycarboxylic aid type superplasticizer (SP) with 2% and 5% by the cement weight is added to the mix. A viscosity enhancement agent (VE) with 0.056% by the cement weight is also added. External bleed water is observed for the mortar with the SP, which exhibited early age expansion. The measurements of autogenous deformation can be influenced by bleed water collecting on the mortar surface before setting. Bleed water is controlled by the VE agent, while bleed water is induced by the SP. The external bleed water is removed through the initial pore space of the mortar surface before the setting of cement, and then transformed into internal bleed water. After the setting, the bleed water may be reabsorbed as self-desiccation occurs, resulting in reduced autogenous shrinkage, or even

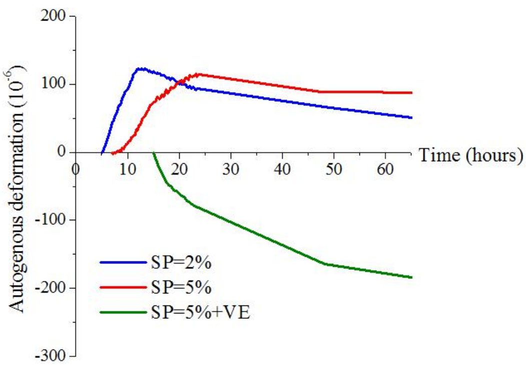


Fig.5 Autogenous deformation of mortars (W/C=0.28)

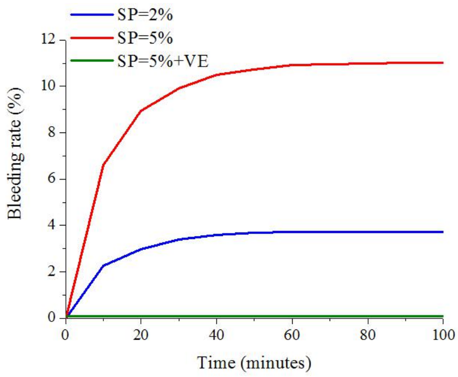


Fig.6 Bleeding rates of mortars (W/C=0.28)

expansion. In addition, although the bleeding rate of the mortar with 2% of the SP is quite smaller than that of mortar with 5% of the SP (Fig.6), the expansion is not so different between the two mortars (Fig.5). Therefore, a little reduction of external bleed water may will not be enough to influence the the entire expansion. One the other hand, it is noted that the time when expansion started increasing is quite different from the time of steep increasing bleed water in mortar surface and the time when the surface bleed water is removed. It may show that reabsorption of bleed water also influences autogenous deformation for long term. Even in the period after all the bleeding water has been consumed, the autogenous deformation may still be affected.

Fluorescence microscope images of mortars at 7 days are shown in Fig.7. The mortars with the SP has a higher fluorescent light intensity, while it is not observed in the images of the mortar with the VE agent. In other words, there are porous regions due to internal bleeding around aggregate particles for the mortars with with the SP, while no internal bleeding is observed in the mortar with the VE agent. It should be noted that the specimens for fluorescence microscope observation have been cured for 7 days, but the internal bleeding is also observed. It means porous region due to the internal bleeding has been left in cement-based mixture for a long time, which may also influence autogenous deformation for long term as mentioned before. However, the expansion is not so different for the two mortars with the SP as mentioned above (Fig.5). The consumed part of internal water, which

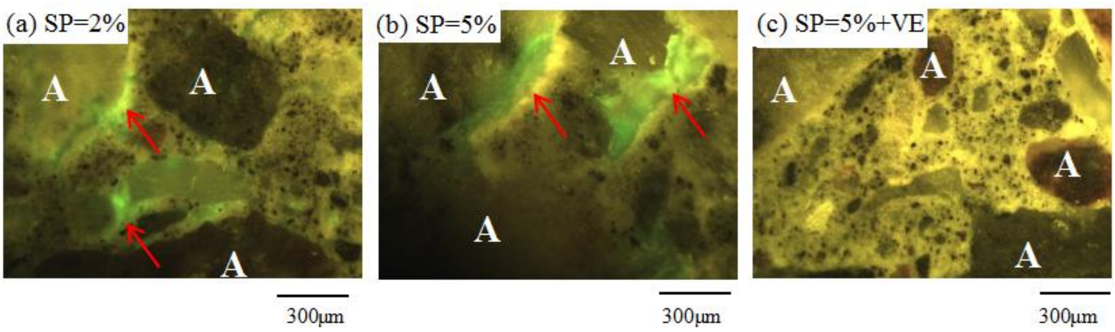


Fig.7 Fluorescence microscope image of mortars at 7 days

(A：Aggregates, Red arrow：bleed water)

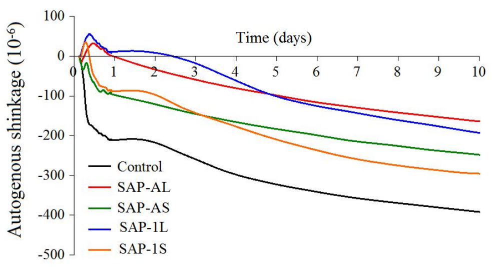


Fig.8 Autogenous deformation of mortars with SAP (W/C=0.28)

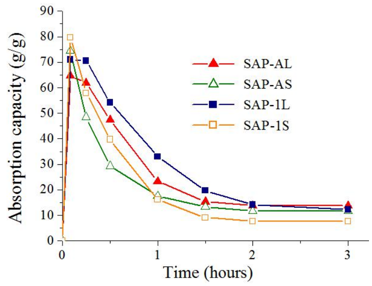


Fig.9 Aabsorption capacity of SAP immersed into $Ca(OH)_2$ solution

is used for compensating self-desiccation, can be assumed as the same amount, due to the similar expansion. Therefore, a part of internal water is not consumed as observed in Fig.7. In other words, there exists a large area in which self-desiccation could not be compensated by the internal water. One of the reason may related to the nonuniform distribution of internal water within the whole cement-based mixture. Furthermore, the internal water could not migrate from internal water reservoirs to the surrounding maturing cement paste, therefore it can not interact with cement pastes successfully.

Autogenous deformation behavior of mortars using each SAP is shown in Fig.8. Changes in absorption capacity of SAPs with time of immersion into saturated calcium hydroxide solution are shown in Fig.9. The released water from SAP affects the expansion at very early ages since it is regarded as internal bleed water. When the internal curing water is consumed or confined, its effect on the expansion decreases so that an apparently change from expansion to shrinkage is observed. Then the increase in autogenous shrinkage of the SAP mortars proceeds at the same rate as that of the control mortars (Fig.8). As for the mortars with large SAPs, expansion continues longer. This behavior may be related to the desorption rate of SAP. When the large SAPs are used, it exhibit a smaller rate of desorption, which affects the longer period of expansion (Fig.8).

5. Effect of gelation of a part of mixing water with SAP on early age properties of cementious materials

Fig.10 shows autogenous deformation after the initial setting time (i.e. deformation is adjusted to zero at the time of initial setting). Here, dosages of SAP-A and SAP-2 are determined to absorb 10% of mixing water. The amount of SAP-2L is also increased to absorb 20% of mixing water. In addition, for comparison, the cement paste with 0.39% SAP-2L to the mass of cement is produced to control the effective water to cement ratio to 0.28. The total water to cement ratio of the mixture of SAP-2L is 0.33, while the total water to cement ratios of other mixtures are 0.28.

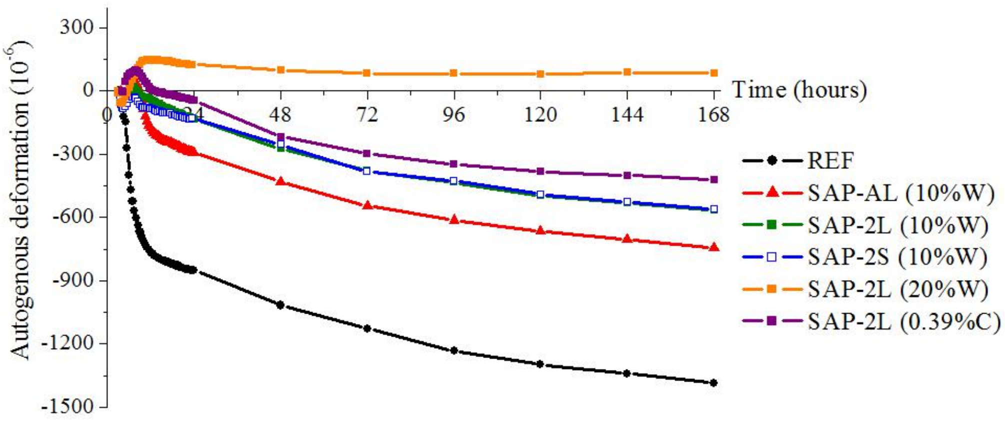


Fig.10 Autogenous deformation of cement pastes after the initial setting time

The mixtures with SAP exhibit significant reduction in shrinkage than that in the REF mixture. In particular expansions observed for several hours after the time zero result in less shrinkage. The mixture with SAP-2L (20%W) has the greatest expansion and the smallest shrinkage, since the SAP absorbs the large amount of mixing water. It is found that the internal water released enough from SAP is effective to compensate for self-desiccation. Furthermore, the mixtures with SAP-AL (10%W), SAP-2L (10%W), SAP-2S (10%W) and SAP-2L (0.39%C) do not exhibit great differences in final shrinkage. In particular for the mixtures of SAP-2L (10%W), SAP-2S (10%W) and SAP-2L (0.39%C), their changes in autogenous shrinkage have a similar trend. In order to reduce self-desiccation and autogenous shrinkage, additional water is added in the mixture with SAP-2L (0.39%C). This leads to the increase in the total water to cement ratio. While for the mixture with SAP-AL (10%W), SAP-2L (10%W), and SAP-2S (10%W), 10% of mixing water is absorbed by SAP to form hydrogel, and the effective water to cement ratio is reduced. Therefore, internal gelation of mixing water with SAP can be used as an effective way to limit self-desiccation and autogenous shrinkage without adding more extra water, which may have an adverse effect in certain properties of the mixture.

Fig.11 shows autogenous deformation after the initial setting time (i.e. deformation is adjusted to zero at the time of initial setting). Here, dosages of SAP-D and SAP-3 are determined to absorb 5% of mixing water. The amount of SAP-D is also increased to absorb 10% of mixing water. In addition, dosages of SAP-D and SAP-3 are also determined about 0.1% and 0.2% by the cement weight, respectively. To control the effective water to cement ratio to 0.55, extra water is necessary for SAP to absorb. The total water to cement ratios of the mixture of SAP-D (0.1%C) and SAP-3 (0.2%C) are 0.58, while the total water to cement ratios of other mixtures are 0.55.

There is obviously change in the REF mortar after the initial setting to 1 day. After 1 day, the autogenous deformation due to shrinkage develops slowly. In contrast to the REF mortars, the mortars with SAP exhibit expansion after the initial setting. The mortars that contain

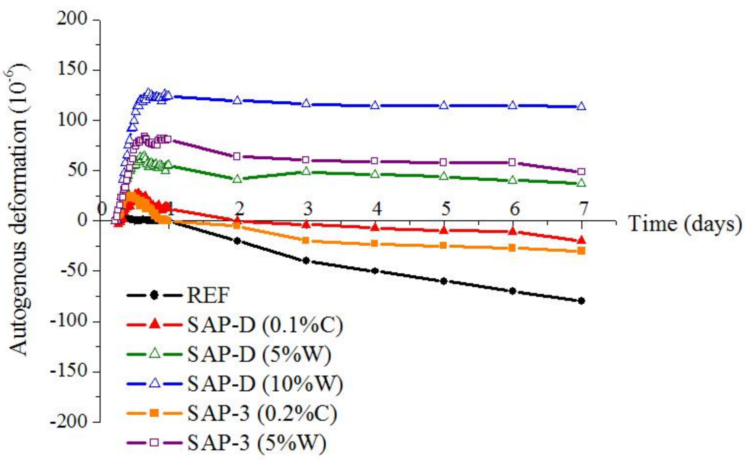


Fig.11 Autogenous deformation of mortars with SAP

water gelled with SAP exhibit expansion. The systems of mortars with extra water for SAP hydrogel shrink continuously after the initial expansion, and the final shrinkage is smaller than the REF mortar. The mortars without extra water for SAP hydrogel maintain their expansions by 7 days. Furthermore, the mortar with SAP-D (10%W) exhibits the greatest expansion, in which SAP absorbs most amount of the mixing water. It is clearly found that the early age expansion is related to the internal water conditions of gelation with SAP and the amount of internal water from SAP. The replacement of mixing water with gelled SAP is more effective than the gelation of extra water with SAP in reducing autogenous shrinkage, even if their amounts of gelation is almost same. The more mixing water SAP absorbed, the larger initial expansion observed. The reduction in autogenous shrinkage results from the initial expansion.

6. Conclusions

Absorption and desorption behaviors of SAP and theirs effects on volume changes in cement-based materials are experimentally investigated. As far as this study is concerned, main conclusions can be summarized as followed:

(1) The modified tea bag method is easier to be affected by agglomeration of SAP particles, which seems to lead to insufficient swollen SAP. The increase in absorption capacity during the test period in the tea bag method is contributed by the retention of interparticle liquid. The graduate cylinder method is considered as a useful way to evaluate absorption capacity in cement environment. All mortars with SAP exhibit expansion. Mitigation of autogenous shrinkage with SAP results form the initial expansion.

(2) The development of plastic viscosity could be related to the water released from SAP. It affects subsequent progress of hydration even in the dormant period. The addition of SAP also affects the development of the plastic viscosity since it changes the amount of

freely available water to alleviate internal friction. The particle sizes of SAP and their initial distribution could affect the initial evolution of internal friction.

(3) The measurements of autogenous deformation is influenced by bleeding before setting. As self-desiccation occurs, the bleed water may be reabsorbed to reduce autogenous shrinkage, or even expansion. Reabsorption of bleed water also influences autogenous deformation for long term. A part of internal water is not consumed to compensate self-desiccation. This is because the internal water is not uniformly distributed within the whole cement-based mixture, or the internal water can not migrate well.

(4) Early age expansion of the mortars with SAP is contributed from the internal water released from the SAP. The magnitude of the expansion and the extent of shrinkage reduction depend on the size of SAPs. The larger SAPs, the greater and the longer period of expansion. Difference in expansive behavior of mortars with SAPs may be related to differences in the initial moisture distribution at the very early ages before the setting of cement.

(5) Gelation of a part of mixing water with SAP can be used as an effective way to mitigate self-desiccation and autogenous shrinkage without adding extra water whereas drying shrinkage is less reduced. The reduction in total volume change with SAP results from the reduction in autogenous shrinkage.The good performance of SAP in mitigating autogenous shrinkage and accelerating hydration obviously result from release of the absorbed water after the dormant period.

(6) The hydrogel of SAP are easier to reduce the porosity, and produce the internal solid skeleton earlier. This promotes the development of electrical resistivity. Gelation of a part of mixing water with SAP results in less decrease in compressive strength in mortars. Effect of SAP on compressive strength reduction in mortars with high water to cement ration is not distinct. The way that a part of mixing water gelled with SAP shows less impact on compressive strength, even the amount of hydrogel is more than that of SAP hydregel with extra water.