

AUTOGENOUS SHRINKAGE OF ALKALI-ACTIVATED FLY ASH-SLAG PASTES WITH AND WITHOUT SAP

Guohao Fang, Wenlin Tu, Yu Zhu and Mingzhong Zhang

Advanced and Innovative Materials (AIM) Group, Department of Civil, Environmental and Geomatic Engineering, University College London, UK

Abstract

This paper presents an experimental study on mitigation of autogenous shrinkage in alkali-activated fly ash-slag (AAFS) pastes by internal curing using superabsorbent polymers (SAP). A series of tests including workability, setting time, mechanical properties and autogenous shrinkage on AAFS pastes with various SAP dosages (0-0.5%) are conducted. The results indicate that the flowability and setting time of fresh AAFS pastes increase with the addition of SAP, while the compressive strength decreases with increasing SAP dosage. The chemical shrinkage and autogenous shrinkage of AAFS pastes are significantly reduced by the addition of SAP. As SAP dosage increases from 0.2% to 0.5%, the chemical shrinkage is reduced by around 18% to 45% while the autogenous shrinkage is decreased by about 76% to 85% compared to that without SAP. Moreover, internal curing using SAP is found to lower the heat peak and shift the peak to the right indicating the slower hydration rate corresponding to the lower chemo-mechanical deformation (chemical shrinkage), which contributes to the mitigation of autogenous shrinkage. Thus, internal curing by means of SAP is an efficient method for mitigating autogenous shrinkage in AAFS pastes.

1. INTRODUCTION

Alkali-activated fly ash-slag (AAFS) is a new blended alkali-activated materials (AAM), which can achieve superior engineering properties under ambient curing condition [1]. Nevertheless, the uncertain long-term durability and insufficient ability against shrinkage and micro-cracking limits the practical application of this material. It was reported that AAFS normally has relatively higher shrinkage such as autogenous shrinkage and drying shrinkage than Portland cement (PC) system [1]. Thus, to avoid significant shrinkage and shrinkage induced early-age cracking, it is vital to mitigate shrinkage of AAFS.

Up to now, various curing methods including external curing (EC) and internal curing (IC) are generally used to reduce or control shrinkage by maintaining the internal relative humidity (RH) [2]. External curing method, such as watering and covering with wet burlap, is found difficult to maintain the internal RH of concrete while internal curing method is considered more effective to retain the internal RH by releasing water from internal curing materials. Lightweight aggregate, shrinkage reducing admixture and superabsorbent polymer (SAP) have been commonly used as IC agents for the PC system. Among them, SAP shows superior absorption and desorption capacity, allowableness of free design of form and size of concrete composite, resistance of concrete to chloride penetration and lower cost.

Recently, some researchers have attempted to investigate the IC of AAM using SAP as IC agent. Oh and Choi [3] and Song et al. [4] studied the effects of IC by means of SAP in Alkali-activated slag (AAS) mortars and concluded that SAP is an effective IC agent leading to a

significant reduction of shrinkage but comparative decrease in compressive strength. However, the potential mitigation of shrinkage in AAFS system with SAP and corresponding mechanisms have not been extensively explored up to now.

The main purpose of this work is to investigate the effect of SAP as an IC agent on chemical and autogenous shrinkage (within 48 h) of AAFS pastes cured at ambient temperature and their fresh and mechanical properties. Firstly, workability, setting time and compressive strength of AAFS pastes with SAP dosages varying from 0% to 0.5% were tested to estimate the effect of SAP on these properties. Chemical shrinkage and autogenous shrinkage in AAFS pastes with and without SAP at early 48 h after casting were then measured to investigate the feasibility of using SAP to mitigate shrinkage. Finally, the reaction kinetic of AAFS pastes with and without SAP was further characterized with the help of isothermal conduction calorimetry (ICC) tests.

2. EXPERIMENTAL PROGRAM

2.1 Raw materials

Class F fly ash (FA) and ground granulated blast-furnace slag (GGBS) were used as precursors. The chemical compositions of FA and GGBS are listed in Table 1. The mean particle size of FA and GGBS is 26.81 and 14.77 μm , respectively. Alkaline activator (AL) was mixed by sodium hydroxide solution (SH) with 10 M and sodium silicate solution (SS) with SiO_2 to Na_2O ratio of 2.0. Since the modified polycarboxylate-based superplasticizers (SPs) have a significant effect on the workability of AAFS [5], it was used to improve the workability of AAFS in this work. In addition, the SAP (AQUASORBTM 3005 S) used in this study was supplied by SNF, UK. It is a cross-linked copolymer of acrylamide and potassium acrylate with irregular particle shape (particle size < 300 μm).

Table 1 Chemical compositions (wt.%) of FA and GGBS

Oxide	SiO_2	Al_2O_3	CaO	MgO	K_2O	Fe_2O_3	TiO_2	Na_2O	SO_3
FA	53.24	26.42	3.65	9.55	2.57	1.65	0.86	0.76	0.56
GGBS	34.30	15	39.40	8	0.38	0.40	0.70	0.45	-

2.2 Determination of SAP adsorption

The absorption capacity of SAP in the pore solution was determined by the ‘tea bag’ method in accordance with a previous study [6]. The portion of mixed solution absorbed by 1g SAP was determined from measuring mass disparity between dry and wetted SAP in the solution after 30 s, 2, 5, 10, 15, 30 and 60 min. A theoretical SAP sorption capacity in the static solution was obtained with possible discrepancies compared to the required IC water. In addition, considering the SAP absorption in a mixing condition, workability test was adopted to obtain the optimal contain of additional water. The optimal amount of additional water of SAP was found to be 12.5 g/g through examining the flow as a function of time, which is most similar value to that of the plain mixture without SAP.

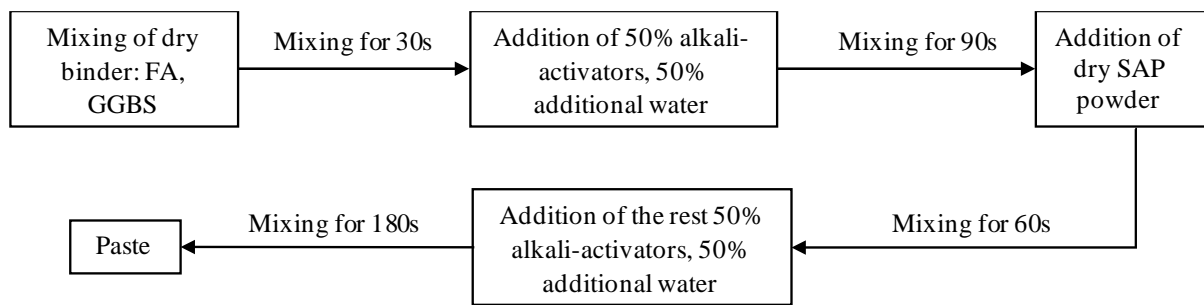
2.3 Mix proportions

A series of AAFS pastes with mix proportions suggested by Fang et al. [7], e.g. slag content of 25%, alkali-activator/binder ratio of 0.4 and 1% by binder mass addition of superplasticiser

for mixture were studied. The IC water of 12.5 g/g SAP was used in the mix design. All mixture proportions are shown in Table 2. Mixtures S0.0 to S0.5 represent different SAP dosages, from 0% to 0.5% by binder mass. Figure 1 shows the mixing process used in this study.

Table 2 Mix proportions (kg/m³) of AAFS pastes

Mix No.	Labels	Binder	FA	GGBS	SS	SH	SPs	SAP	Water
0	S0.0	400	300	100	106.5	53.5	4	0	0
1	S0.2	400	300	100	106.5	53.5	4	0.8	10
2	S0.3	400	300	100	106.5	53.5	4	1.2	15
3	S0.4	400	300	100	106.5	53.5	4	1.6	20
4	S0.5	400	300	100	106.5	53.5	4	2	25



*For mixture of control samples without SAP, the total mixing time is reduced by 60s

Figure 1: Mixing process for AAFS pastes

2.4 Test methods

The workability of pastes was tested using flow table test following ASTM C1437-01, while the setting time was measured according to ASTM C191-13. The compressive strength tests were carried out using a multifunctional computerised control console machine according to BS EN 12390-3:2009. The chemical shrinkage tests were performed using dilatometry method suggested by ASTM C1608-12. The autogenous shrinkage tests were conducted using linear measurements by monitoring the dimension change of the paste samples cast in the rigid mould.

3. RESULTS AND DISCUSSION

As seen in Figure 2, the flowability of AAFS specimens is largely improved with the increase of SAP dosage. For example, the flow is increased from 112 to 145 when the SAP dosage increases from 0.2% (S0.2) to 0.5% (S0.5). This can be explained by the fact that with the addition of SAP, addition water is added in the mixtures. As the SAP dosage increases, more additional water is incorporated. Regarding the absorption rate of SAP, the mixed alkali-activator, particularly SS is diluted with a lower resultant viscosity. Consequently, less cohesive tissue is formed in the mixture, which contributes to an ameliorative workability. Similarly, the addition of SAP increases the setting time of AAFS pastes (see Figure 3). The addition of IC

water could delay the chemical reaction in AAFS pastes due to the formation of swollen SAP hydrogel and further hydration reaction. It is worth pointing out that there could be a potential change of AL/B ratio caused by available water inside SAP particles involving in the chemical reaction. This aspect will be discussed further below.

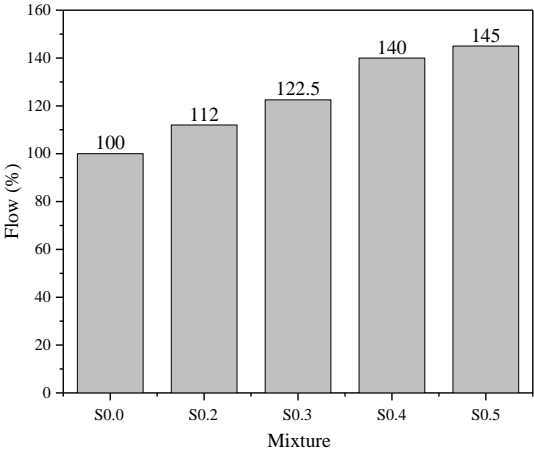


Figure 2: Flow value of AAFS pastes with different SAP dosages

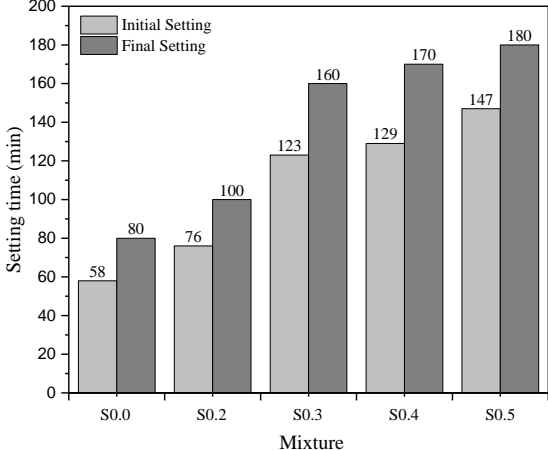


Figure 3: Setting time of AAFS pastes with different SAP dosages

Figure 4 shows the effect of SAP dosage on compressive strength of AAFS pastes at various curing ages. The compressive strength is decreased with the addition of SAP regardless of curing age. In detail: the compressive strength loss from S0.0 to S0.2 is approximately 20%, while the reduction in compressive strength from S0.2 to S0.4 is not obvious followed by a significant decrease when the SAP dosages increases from 0.4% (S0.4) to 0.5% (S0.5). This implies that there may be a combined effect between strength loss and gain, as SAP particles could arguably play the role as crack arrestors to improve compressive strength. It is worth noting that the difference between compressive strength of specimens decreases in time, which indicates the initial disparity in porosity could be partially compensated by further chemical reaction. Additionally, it can be found that the mixtures of S0.2, S0.3 and S0.4 meet the performance criteria of engineering application, i.e., a 28-d compressive strength of 35 MPa and more according to ACI 318M-05.

Chemical shrinkage is recognised as one of the main causes of early-age autogenous shrinkage owing to the voids generated by volumetric discrepancy between chemical reactants and products in matrix. As shown in Figure 5, the chemical shrinkage is obviously reduced as SAP dosage increases. When SAP dosage increases from 0.2% to 0.5%, the chemical shrinkage is reduced by around 18% to 45% compared to the control mixture without SAP. The mitigation of chemical shrinkage in AAFS system can be attributed to the IC effect of SAP, since the additional water released from swollen SAP particles can impede the early-age chemical reaction and refine the pore structure.

Figure 6 shows the autogenous shrinkage evolution of AAFS pastes with different SAP dosages. The autogenous shrinkage increases rapidly during the first few hours followed by a slight increase and a dormant period. The results reveal a substantial autogenous shrinkage reduction of 76-85% with 0.2-0.5% SAP addition compared to S0.0, which can be ascribed to the decrease of self-desiccation caused by a lower level of induced capillary pressure during

the IC process. A dramatic mitigation of autogenous shrinkage can be observed in S0.2 and S0.3, whereas the shrinkage mitigation is less significant when SAP dosage is more than 0.3%. This indicates that an optimal SAP dosage is 0.3% regarding shrinkage mitigation efficiency.

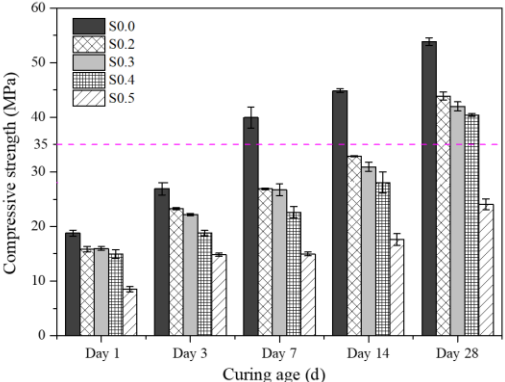


Figure 4: Compressive strength of AAFS pastes with different SAP dosages

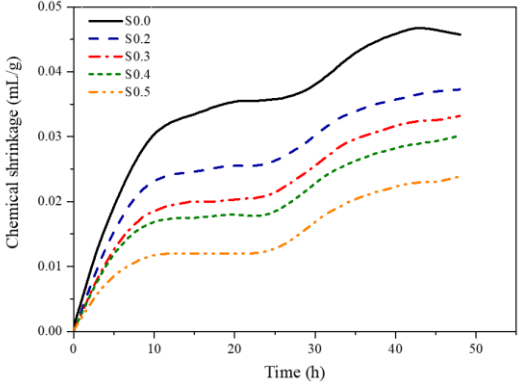


Figure 5: Chemical shrinkage of AAFS pastes with different SAP dosages

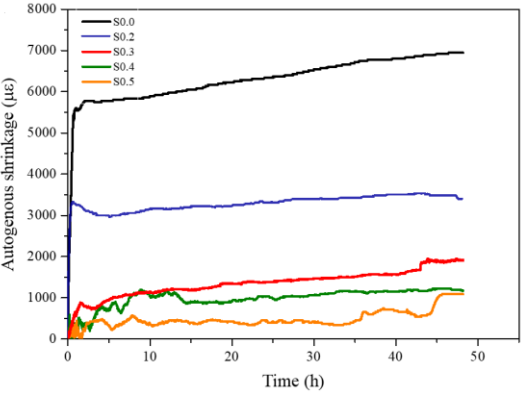


Figure 6: Autogenous shrinkage of AAFS pastes with different SAP dosages

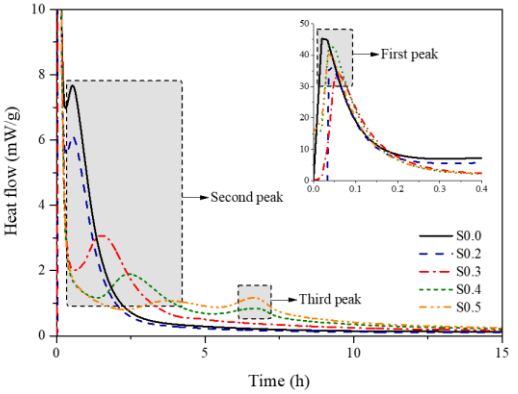


Figure 7: Heat flow of AAFS pastes with different SAP dosages

Figure 7 shows the ICC results that can be used to explain the reaction kinetic of AAFS pastes with and without SAP. It can be seen that the first peak appeared in heat flow curves at the very beginning does not reflect the actual chemical reaction since it shows a physical phenomenon, whereas the second peak indicates the main reaction of the formation of reaction products. As the SAP dosage increases from 0.2% (S0.2) to 0.5% (S0.5), the ultimate heat flow of second peak decreases significantly from 6.04 mW/g to 1.08 mW/g, which indicates that the inclusion of SAP could impede the early-age chemical reaction of the paste by providing additional water. Also, the acceleration period is retarded from about 1 to 4 h and shifted to the right, which implies the deceleration of initial alkali-reaction. This can be attributed to the absorption characteristics of SAP. Besides water, some alkaline ions could be absorbed by SAP as well during the first few hours after mixing. The implication is that the concentration of alkali-activator could be affected by absorption behaviour of SAP, thus leading to delay of the main peak. This is consistent with the setting time results that a longer setting time occurs when SAP dosage increases.

4. CONCLUSIONS

In this study, the feasibility of using SAP as internal curing agents to mitigate the autogenous shrinkage in AAFS pastes cured at ambient temperature while maintaining the acceptable engineering properties including workability, setting time and compressive strength is investigated. Based on the experimental results, the main conclusions can be drawn as follows:

- Flowability and setting time of AAFS pastes increase with the addition of SAP, while the compressive strength is reduced with increasing SAP dosage. The compressive strength is decreased by 20% when 0.2% SAP (by binder mass) is added into the mixture, but slightly decreases as the SAP dosage increases from 0.2% to 0.4%.
- Chemical shrinkage and autogenous shrinkage of AAFS pastes are significantly reduced by the addition of SAP. As SAP dosage increases from 0.2% to 0.5% the chemical shrinkage is reduced by around 18% to 45% while the autogenous shrinkage is decreased by about 76% to 85%.
- The addition of SAP lowers the heat peak of the AAFS pastes and leads to a shift of the peak to the right, which corresponds to the slower hydration rate and lower chemical shrinkage resulting in a reduction in autogenous shrinkage.
- Internal curing by means of SAP is an effective strategy to mitigate the autogenous shrinkage in AAFS pastes. The optimal SAP dosage is found to be 0.3%.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the financial support of the Royal Society (IE150587) and EPSRC (EP/R041504/1). The financial support provided by University College London (UCL) and China Scholarship Council (CSC) to the first author is greatly appreciated.

REFERENCES

- [1] Bernal, S.A., Provis, J.L., Walkley, B., San Nicolas, R., Gehman, J.D., Brice, D.G., Kilcullen, A.R., Duxson, P. and van Deventer, J.S.J., 'Gel nanostructure in alkali-activated binders based on slag and fly ash, and effects of accelerated carbonation', *Cem. Concr. Res.* **53** (2013) 127-144.
- [2] Liu, J., Shi, C., Ma, X., Khayat, K.H., Zhang, J. and Wang, D., 'An overview on the effect of internal curing on shrinkage of high performance cement-based materials', *Constr. Build. Mater.* **146** (2017) 702-712.
- [3] Oh, S. and Choi, Y.C., 'Superabsorbent polymers as internal curing agents in alkali activated slag mortars', *Constr. Build. Mater.* **159** (2018) 1-8.
- [4] Song, C., Choi, Y.C. and Choi, S., 'Effect of internal curing by superabsorbent polymers – Internal relative humidity and autogenous shrinkage of alkali-activated slag mortars', *Constr. Build. Mater.* **123** (2016) 198-206.
- [5] Jang, J.G., Lee, N.K. and Lee H.K., 'Fresh and hardened properties of alkali-activated fly ash/slag pastes with superplasticizers', *Constr. Build. Mater.* **50** (2014) 169-176.
- [6] Schröfl, C., Mechtcherine, V. and Gorges, M., 'Relation between the molecular structure and the efficiency of superabsorbent polymers (SAP) as concrete admixture to mitigate autogenous shrinkage', *Constr. Build. Mater.* **42** (2012) 865-873.
- [7] Fang, G., Ho, W.K., Tu, W. and Zhang, M., 'Workability and mechanical properties of alkali-activated fly ash-slag concrete cured at ambient temperature', *Constr. Build. Mater.* **172** (2018) 476-487.