

Internal Curing by SAP in Ultra-High Strength Concrete with Cement-Silica Fume-Fly Ash Binder

J. Liu and C. Shi

Key Laboratory for Green & Advanced Civil Engineering Materials and Application Technology of Hunan Province, College of Civil Engineering, Hunan University, Changsha, China;

X. Ma

Henan University of Urban Construction, Pingdingshan, Henan, China

ABSTRACT

Super-absorbed polymer (SAP) is an effective internal curing materials for reducing autogenous shrinkage and improving cracking resistance of ultra-high-strength concrete (UHSC). This study investigated the compressive strength, shrinkage properties of UHSC with cement–silica fume–fly ash binder. The composition of the binder was designed using seven-batch factorial design method. The relationships between the binder composition and the properties were expressed in contours. Results showed that, silica fume could improve the compressive strength and total shrinkage of UHSC. However fly ash reduced the compressive strength and total shrinkage of UHSC to certain extent. On the other hand, under the internal curing of SAP, the silica fume and fly ash demonstrated positive synergistic effects on the compressive strength. At the early age of hydration, the effectiveness of internal curing first increases and then decreases with the increase of fly ash and silica fume content. However, at the later age of hydration, the effectiveness of internal curing by SAP reduced because of the pozzolanic activity of silica fume and fly ash.

Keywords: Ultra high-strength concrete; Internal curing; Shrinkage; Compressive strength; Super-absorbed polymer (SAP)

1.0 INTRODUCTION

Ultra-high strength concrete (UHSC) is a composite material with superior static and dynamic mechanical properties, and excellent durability (Shi, Wu *et al.* 2015, Wang, Shi *et al.* 2015, Wu, Shi *et al.* 2016). Because of its high content of cementitious materials and very low water-to-binder ratio (w/b), the self-desiccation phenomenon is very serious (Lura, Jensen *et al.* 2003, Ghafari, Ghahari *et al.* 2016, Liu, Shi *et al.* 2017). If the early age shrinkage of UHSC cannot be effectively controlled, the self-stress development under constraint conditions may induce cracking and impair the properties of concrete (Wu, Farzadnia *et al.* 2017). Conventional external curing methods, such as watering and covering with wet burlap, are difficult to have obvious effects due to a relatively low surface porosity of UHSC. Internal curing is thought to be a very effective way to retain the internal relative humidity (RH) of concrete by releasing water of internal curing materials (Lura 2003). Lightweight aggregate (LWA) proposed by Philleo (Philleo 1991) and super-absorbent polymer (SAP) proposed by Jensen (Jensen and Hansen 2001) are two frequently-used internal materials. Rice husk ash (RHA) has been used as an internal curing material for UHPC in recently years (Tuan, Ye *et al.* 2010). In addition, people have also found several

other internal curing materials, such as bottom ash (Wyrzykowski, Ghourchian *et al.* 2016) and cenospheres (Liu, Wang *et al.* 2017). Internal curing was firstly defined in ACI 308-2001 (308R 2001). RILEM TC 225 was set up in 2007 to promote research and application of SAP. Many studies have been carried out in the recent years about the effects of SAP or LWA on the shrinkage of concrete (Bentz and Weiss 2011, Mechtcherine and Reinhardt 2012).

SAPs are cross-linked polyelectrolytes which swell upon contact with water or aqueous solutions and result in the formation of hydrogel (Mechtcherine and Reinhardt 2012). They include acrylamide/acrylic acid copolymer and polyacrylic acid. The main driving force for the swelling of SAPs is the osmotic pressure that is proportional to the concentration of ions in the aqueous solution (Kang, Hong *et al.* 2017). Thus, the absorption capacity of SAPs is strictly dependent on the concentration of ions in the solution medium (Mechtcherine and Reinhardt 2012). SAPs have water absorption capacity of up to 5000 times of their own mass (Jensen and Hansen 2001). Internal curing by SAPs is based on the release of water from a reservoir within the SAP into the microstructure; thereby the cement matrix maintains a high relative humidity (RH) over time. Therefore, SAPs can effectively inhibit the autogenous shrinkage (Jensen

and Hansen 2001, Jensen and Hansen 2002) and the onset of cracking (Craeye, Geirnaert *et al.* 2011, Beushausen and Gillmer 2014). The effectiveness of SAPs is related to its dosage (Liu, Shi *et al.* 2017, Ma, Liu *et al.* 2017), particle size (Lura, Durand *et al.* 2006, Esteves 2009) and water-to-binder ratio of the matrix (Igarashi and Watanabe 2006, Zhutovsky and Kovler 2017). However, the incorporation of SAPs has adverse effects on some properties of cement-based materials, such as the decrease of mechanical performance because of the generated pores (Farzarian, Teixeira *et al.* 2016), and the increase of drying shrinkage (Ma, Liu *et al.* 2017).

In addition, the internal curing may be influenced by the addition of SCMs in UHSC (Klemm and Sikora 2012). The addition of SAP (0.70% by mass of cement) could not completely prevent autogenous shrinkage of cement paste incorporation of SF (Igarashi and Watanabe 2006). Snoeck *et al.* (Snoeck, Jensen *et al.* 2015) showed that the size of SAP A (with mean diameter of 100 μm) is preferable in restraining autogenous shrinkage compared to the size of SAP B (with mean diameter of 477 μm) when the cement paste contains different mineral admixtures (fly ash and slag). At the same time, due to the pozzolanic effect, autogenous shrinkage rate could increase quickly in the later period of hydration (28d). As a result, the SAP dosage should be increased to mitigate the effect of pozzolanic activity of SCMs that would contribute to enhancing long-term cement hydration. Therefore, this paper uses ternary cementitious materials (cement-silica fume-fly ash system), analyse the relationship between the composition and properties under the condition of internal curing and without internal curing. The relationship between mineral admixture composition and internal curing efficiency would be established.

2.0 EXPERIMENTAL

2.1 Raw Materials

The cementitious materials used in this work include P.I. 42.5 Portland cement, silica fume, slag and fly ash. Their physical properties and chemical composition are shown in Tables 1 and 2. Fine aggregate (natural sand) with particle size of 0 to 2.36 mm was used. Its fineness modulus and apparent density were 2.7 and 2610 kg/m^3 , respectively.

SAP is a kind of angular covalently cross-linked acrylamide/acrylic acid copolymer. Its particle size is shown in Fig. 1. The water absorption of SAP is 210 g/g in tap water, but only 5.4 g/g in the cement suspension liquid with w/c of 10.

2.2 Mixture Proportion Design

In this paper, the independent factors are proportions of different components of cementitious materials which is cement, silica fume and fly ash. In addition,

the proportions of the different factors must sum to 100%. According to relevant reference (Cornell 2011), and it is suitable to use simplex-centroid design to analysis the effects of different of cementitious materials on compressive strength and total shrinkage, especially in the condition of internal curing.

This method has been successfully used to study how the ternary cementitious composition affected strength or to predict the strength of ternary cementitious materials and alkali-aggregate reaction expansion. In this study, the seven-batch factorial design was used for the composition of binders. The response contour plots for the ternary cementitious system can be obtained in a ternary diagram.

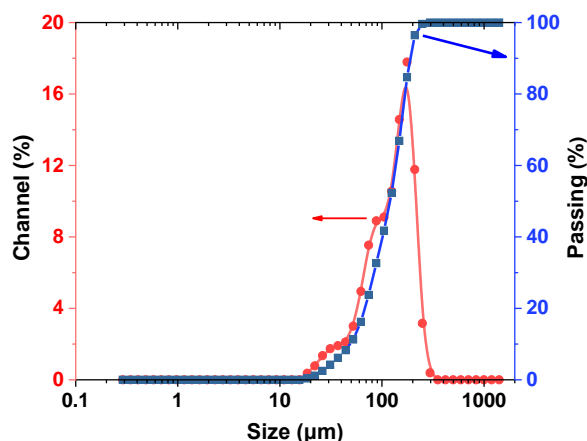


Fig. 1. Particle size distributions of SAP

Table 1. Chemical composition and physical properties of cement, silica fume and fly ash

	Cement	Silica fume	Fly ash
SiO ₂	20.76	93.9	54.29
Al ₂ O ₃	4.58	-	32.55
Fe ₂ O ₃	3.27	0.59	5.53
CaO	62.13	1.85	1.34
MgO	3.13	0.27	2.56
SO ₃	2.8	-	-
Na ₂ O _{eq}	0.57	-	-
f-CaO	0.76	-	-
R ₂ O	-	1.03	0.19
Loss	1.86	0.3	3.19

According to the method of simplex-centroid design (Cornell 2011), the binder compositions of UHSCs are shown in Fig. 2 and Table 3. The water to binder (W/b) ratio of reference samples without SAP, as annotated 1 to 7, was 0.18. The dosage of SAP of the SAP group, as annotated P1 to P7, was 0.6% (wt) of cementitious materials. Extra w/b was 0.04 due to the addition of SAP. The sand to binder ratio of all specimens were 1.1. Polycarboxylate-based superplasticizer (SP) with water reduction capability of 25% was used. The amount of superplasticizer was

adjusted to meet the same initial slump flow (200 ± 10 mm). Mixing program of materials was carried out according to (Ma, Liu *et al.* 2017). Water, superplasticizer and silica fume were firstly mixed in order to improve the ability to disperse the silicate fume particles.

Table 2. Physical properties of Portland cement

Density (kg/m ³)		3150
Specific Surface Area (m ² /kg)		348
Setting Time (Min)	Initial	152
	Final	212
Flexural Strength (MPa)	3d	5.6
	28d	8.6
Compressive Strength (MPa)	3d	28.6
	28d	51.2

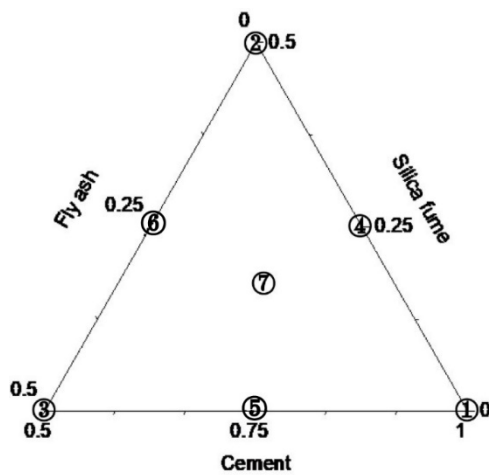


Fig. 2. Ternary cementitious materials according to simplex-centroid design

Table 3. Binder compositions of UHSC (By weight)

No.	Cement	Silica fume	Fly ash
1	100	0	0
2	50	50	0
3	50	0	50
4	75	25	0
5	75	0	25
6	50	25	25
7	73.3	16.7	16.7

2.3 Testing Methods

Compressive Strength

The strength testing was carried out according to EN 196-1-2005. The size of sample was 40 mm x 40 mm x 40 mm. Each batch had three samples. All samples molded were kept in the condition of 20°C and 98% RH for 24 h. They were then demoulded and continued to be cured in the above condition until at the age of 3 d and 28 d.

Shrinkage Deformation

The shrinkage deformation of UHSC was measured according to ASTM C490/C490M. Fresh concrete was cast into 25 x 24 x 275mm molds. After casting, concrete specimens were cured in standard curing room ($T=20\pm 1^\circ\text{C}$ and $\text{RH}\geq 98\%$) for 24 h. After that, specimens were transferred into a chamber with a temperature of $20\pm 2^\circ\text{C}$ and relative humidity of $50\pm 5\%$. The original length and weight of specimens were measured. The length and weight of specimens at 1, 3, 7, 14, 28, 56, and 91 d were recorded to evaluate drying shrinkage of UHSC.

3.0 RESULTS AND DISCUSSIONS

3.1 Compressive Strength

Figures 3 and 4 show that the compressive strength of UHSC with cement-silica fume-fly ash binder at 3d and 28d. The strength of UHSC increases with the increase of silica fume content. When the content of silica fume increases from 0% to 25%, the 3d compressive strength of UHSC increases from 77.2 MPa to 85.9 MPa, and the 28d compressive strength of UHSC increases from 111.1 MPa to 130.4 MPa. The increase in compressive strength is result from the pozzolanic effect and micro-aggregate effect of silica fume increase the compressive strength of UHSC. In the early stage of hydration, the amorphous SiO_2 reacts with the calcium hydroxide produced by cement hydration to form C-S-H, which increases the strength of UHSC (Juenger and Siddique 2015). However, when the content of silica fume exceeds 25%, the 3 d and 28 d compressive strength of UHSC would reduce with the increase of content of silica fume. This may be because when the silica fume content is too large, the fluidity of the concrete is decreased, and the porosity of the concrete is increased, thereby reducing the strength of concrete.

At 3 d, the incorporation of fly ash reduces the strength of UHSC. In the initial period of hydration, cement hydration is the main hydration reaction. The bonding of fly ash particles and cement hydration product is weak at early ages (Lothenbach, Scrivener *et al.* 2011), so the incorporation of fly ash reduces the early strength of the concrete. At the age of 28 d, with the increase of fly ash content, the strength of UHSC firstly increases and then decreases. This is mainly because the PH value of the pore solution of the concrete increases with the hydration of the cement. It would break glassy fly ash, and the pozzolanic reaction of fly ash would become a major chemical reaction, further increasing the strength of concrete (Hannesson, Kuder *et al.* 2012). However, when the fly ash content exceeds 25%, the 28 d strength of UHSC decreases slightly because of the reaction degree of fly ash is low.

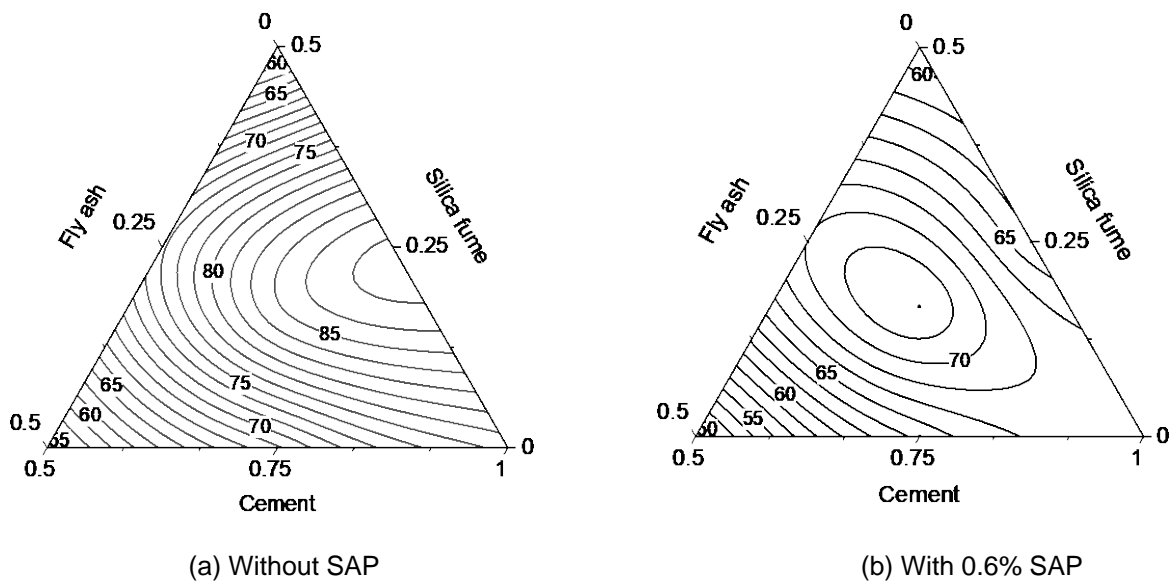


Fig. 3. Compressive strength of UHSC at 3 d

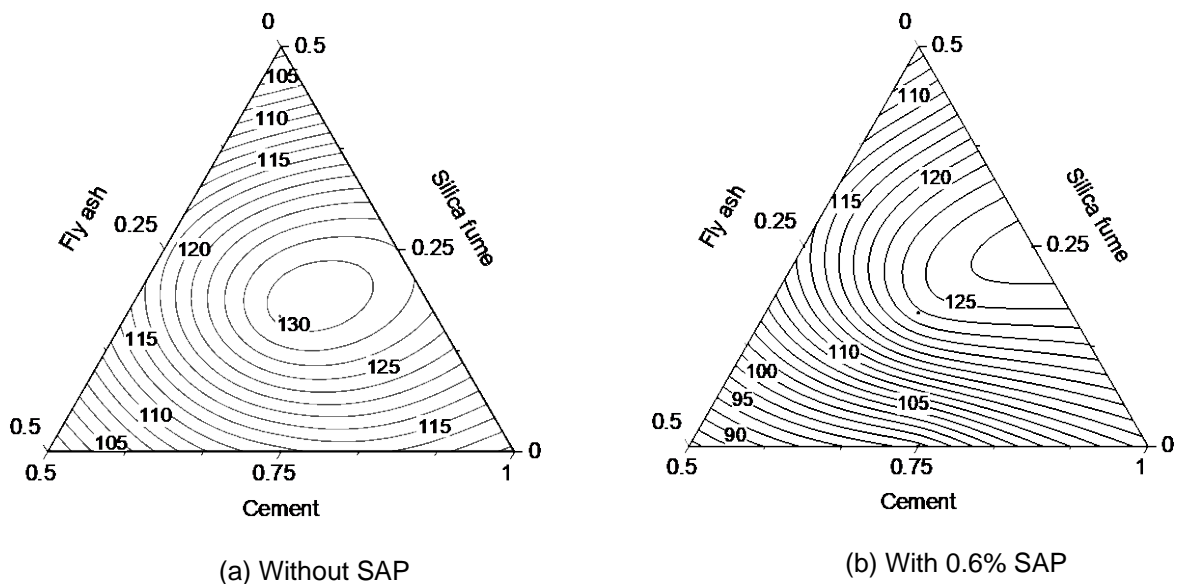


Fig. 4. Compressive strength of UHSC at 28 d

In general, adding SAP can reduce the compressive strength of UHSC, especially at 3 d. As the age increases, the strength of UHSC with SAP increases gradually, reaching a level that is basically consistent with the reference. In addition, the addition of SAP could cause some change under the different ages. At 3 d, the compressive strength of UHSC with 0.6% SAP also has a peak, as shown in contour figure. However, the peak value is transferred from a low content to a high content of fly ash. At 28 d, the peak is retransferred to low content of fly ash. It is shown that, the addition of SAP could be beneficial for the hydration of fly ash at the early ages.

3.2 Shrinkage Properties

Figure 5 shows that the total shrinkage of UHSC with and without of SAP within 56 d. As reported in other research (Shi, Wang *et al.* 2015, Ghafari, Ghahari *et*

al. 2016), the addition of silica fume could increase the shrinkage, and fly ash could reduce the shrinkage. The addition of SAP could restrain the shrinkage development of UHSC with cement-silica fume-fly ash binder. The contour figure could obviously show the total shrinkage varies with component of binder, as shown in Figs. 6 and 7.

At 3 d and 28 d, the addition of silica fume increases the total shrinkage greatly. However, the addition of fly ash could restrain the shrinkage development of UHSC. In addition, at 3 d, there is a peak value of shrinkage under the ternary component of binder, when the content of silica fume is within the range of 15% to 20%, and the content of fly ash within the range of 15% to 25%, as shown in Fig. 6a. However, we cannot see this phenomenon after the addition of SAP, as shown in Fig. 6b, although the total shrinkage also increases with the increase of silica fume content

and reduces with the increase of fly ash content. There are also a valley value when the fly ash content is high. At 28 d, both the UHSC specimens with and without SAP have a peak value, but the two peak value are not in the same binder component. The

peak value in UHSC specimens with SAP more able to appear when the content of silica fume is within in the range of 25% and the fly ash in the range of 15% to 25%, which is high than the UHSC specimens without SAP.

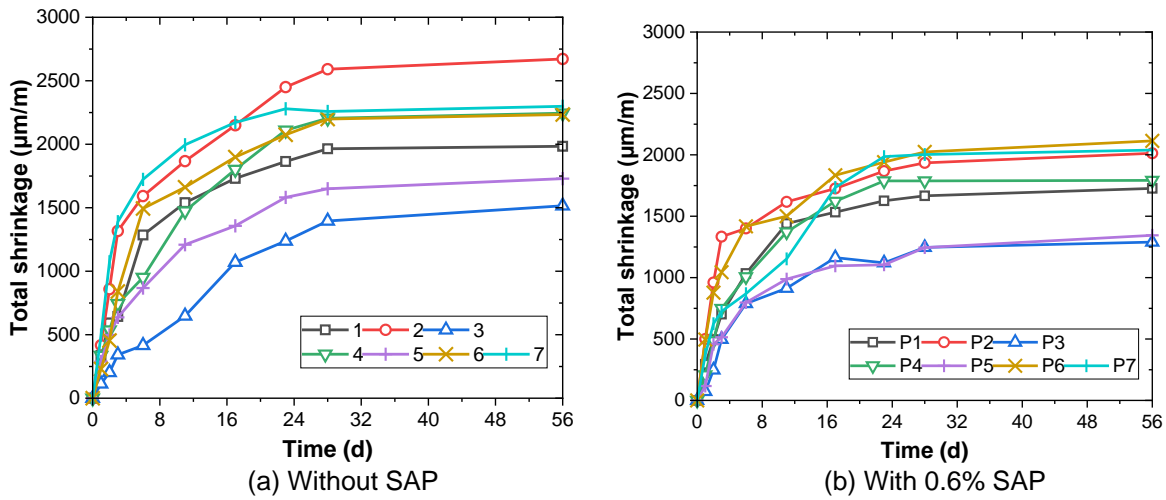


Fig. 5. Total shrinkage of UHSC with or without SAP

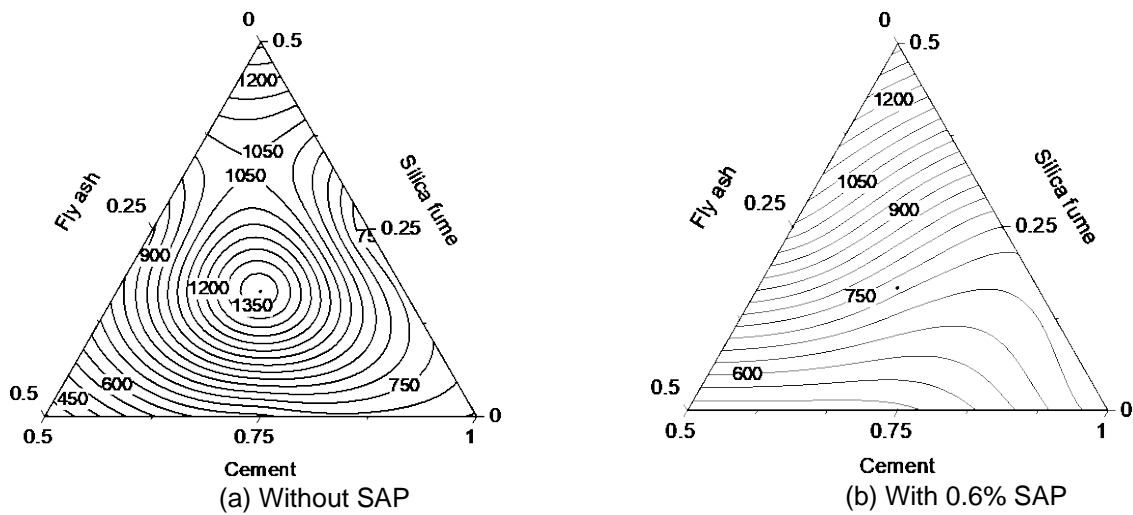


Fig. 6. Total shrinkage of UHSC at 3d

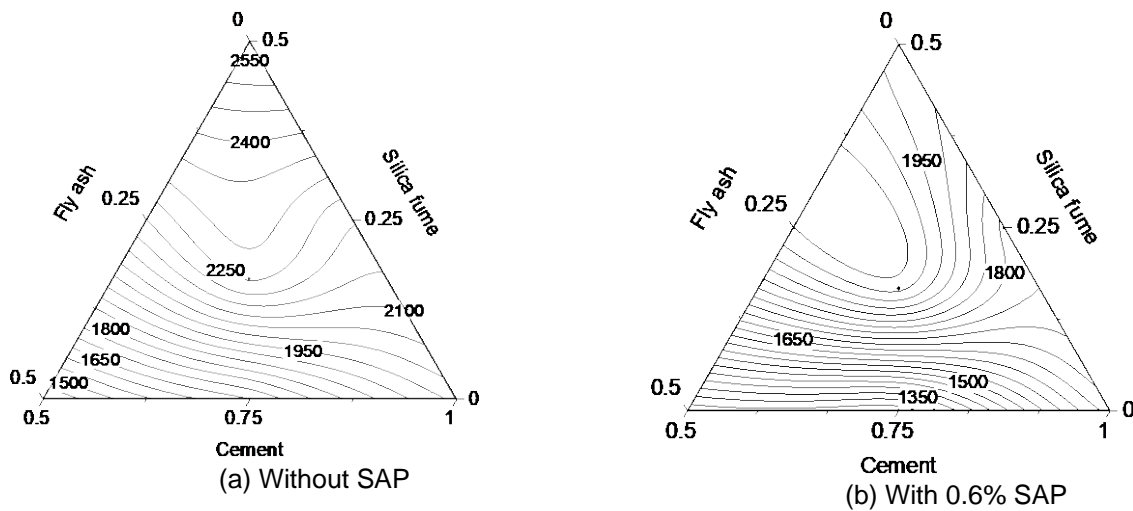


Fig. 7. Total shrinkage of UHSC at 28d

3.3 Effectiveness of internal curing

The main purpose of internal curing is to reduce shrinkage while ensuring that the strength is equivalent. In order to properly characterize its effectiveness, this paper defines the internal curing effectiveness to correctly assess the effect of SAP on the shrinkage of UHSC with different binder component, as shown in Eq. 1. Calculate its internal curing effectiveness by Equation 1, and the final result is shown in Fig. 8. At 3 d, the effectiveness of internal curing varies greatly with the component of the binder material (-40% to 40%), and negative values represent side effects. In other words, under certain component, the addition of SAP can increase the shrinkage, which may be related to the decrease of the actual water-binder ratio caused by SAP absorbing water. In general, the effectiveness of internal curing first increases and then decreases with the increase of fly ash and silica fume content. Among them, in the case of a mixture of 12.5% fly ash and 12.5% silica fume, the internal curing effectiveness is highest.

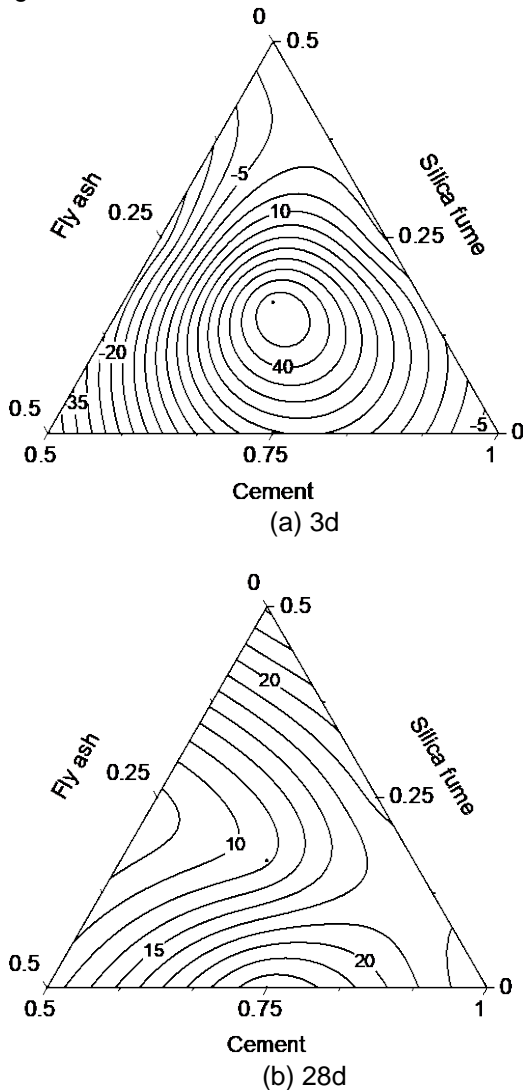


Fig. 8. Effectiveness of internal curing at different ages

At 28 days, All UHSC specimens under different binder component can achieve a certain internal curing effectiveness. With the increase of the amount of silica fume, the effectiveness of internal curing changes little. However, with the increase of fly ash, the effectiveness of internal curing gradually decreased. The effectiveness of internal curing under low-level fly ash and low-silica fume conditions is relatively good, which is related to the pozzolanic activity of silica fume and fly ash. At the early age of hydration, the effectiveness of internal curing by SAP increased with the increase of fly ash content, and reduced with the increase of silica fume content. However, at the later age of hydration, the effectiveness of internal curing by SAP reduced because of the pozzolanic activity of silica fume and fly ash.

$$\Delta \varepsilon = \frac{\varepsilon_{sh}^{IC} - \varepsilon_{sh}^0}{\varepsilon_{sh}^0} \quad (1)$$

Where: $\Delta \varepsilon$ is internal curing effectiveness, ε_{sh}^{IC} is total shrinkage of UHSC with internal curing, ε_{sh}^0 is total shrinkage of UHSC without internal curing.

4.0 CONCLUSIONS

From Based on the results of shrinkage and compressive strength, the following conclusions can be drawn:

- 1) Silica fume could improve the compressive strength of UHSC. However fly ash reduced the compressive strength of UHSC to certain extent. In general, adding SAP can reduce the compressive strength of UHSC, especially at 3d. However, the addition of SAP could be beneficial for the compressive strength of fly ash at the early ages. As the age increases, the strength of UHSC with SAP increases gradually, reaching a level that is basically consistent with the reference.
- 2) Silica fume could increase total shrinkage of UHSC. However fly ash reduced the total shrinkage of UHSC to certain extent. The peak value of shrinkage in UHSC specimens with SAP more able to appear when the content of silica fume is within in the range of 25% and the fly ash in the range of 15% to 25%, which is high than the UHSC specimens without SAP.
- 3) At the early age of hydration, the effectiveness of internal curing first increases and then decreases with the increase of fly ash and silica fume content. Among them, in the case of a mixture of 12.5% fly ash and 12.5% silica fume, the internal curing effectiveness is highest. However, at the later age of hydration, the effectiveness of internal curing by SAP reduced because of the pozzolanic activity of silica fume and fly ash.

Acknowledgement

The authors gratefully acknowledge the financial supports from the National Science Foundation of China under project Nos. U1305243, U1504508 and 51378196.

References

- 308R, A. (2001). Guide to Curing Concrete, American Concrete Institute.
- Bentz, D. P. and W. J. Weiss (2011). Internal curing: a 2010 state-of-the-art review, US Department of Commerce, National Institute of Standards and Technology.
- Beushausen, H. and M. Gillmer (2014). "The use of superabsorbent polymers to reduce cracking of bonded mortar overlays." *Cement & Concrete Composites* **52**: 1-8.
- Cornell, J. A. (2011). Experiments with mixtures: designs, models, and the analysis of mixture data, John Wiley & Sons.
- Craeye, B., M. Geirnaert and G. De Schutter (2011). "Super absorbing polymers as an internal curing agent for mitigation of early-age cracking of high-performance concrete bridge decks." *Construction and Building Materials* **25**(1): 1-13.
- Esteves, L. P. (2009). Internal curing in cement-based materials.
- Farzarian, K., K. P. Teixeira, I. P. Rocha, L. D. Carneiro and A. Ghahremaninezhad (2016). "The mechanical strength, degree of hydration, and electrical resistivity of cement pastes modified with superabsorbent polymers." *Construction and Building Materials* **109**: 156-165.
- Ghafari, E., S. A. Ghahari, H. Costa, E. Julio, A. Portugal and L. Duraes (2016). "Effect of supplementary cementitious materials on autogenous shrinkage of ultra-high performance concrete." *Construction and Building Materials* **127**: 43-48.
- Hannesson, G., K. Kuder, R. Shogren and D. Lehman (2012). "The influence of high volume of fly ash and slag on the compressive strength of self-consolidating concrete." *Construction and Building Materials* **30**: 161-168.
- Igarashi, S.-i. and A. Watanabe (2006). Experimental study on prevention of autogenous deformation by internal curing using super-absorbent polymer particles. Volume changes of hardening concrete: testing and mitigation. Proceedings of the international RILEM conference, Denmark.
- Jensen, O. M. and P. F. Hansen (2001). "Water-entrained cement-based materials I. Principles and theoretical background." *Cement and Concrete Research* **31**(4): 647-654.
- Jensen, O. M. and P. F. Hansen (2002). "Water-entrained cement-based materials II. Experimental observations." *Cement and Concrete Research* **32**: 973-978.
- Juenger, M. C. G. and R. Siddique (2015). "Recent advances in understanding the role of supplementary cementitious materials in concrete." *Cement and Concrete Research* **78**: 71-80.
- Kang, S. H., S. G. Hong and J. Moon (2017). "Absorption kinetics of superabsorbent polymers (SAP) in various cement-based solutions." *Cement and Concrete Research* **97**: 73-83.
- Klemm, A. and K. Sikora (2012). The effect of cement type on the performance of mortars modified by superabsorbent polymers. Concrete Repair, Rehabilitation and Retrofitting III: 3rd International Conference on Concrete Repair, Rehabilitation and Retrofitting, ICCRRR-3, 3-5 September 2012, Cape Town, South Africa, CRC Press.
- Liu, F. J., J. L. Wang, X. Qian and J. Hollingsworth (2017). "Internal curing of high performance concrete using cenospheres." *Cement and Concrete Research* **95**: 39-46.
- Liu, J., C. Shi, X. Ma, K. H. Khayat, J. Zhang and D. Wang (2017). "An overview on the effect of internal curing on shrinkage of high performance cement-based materials." *Construction and Building Materials* **146**: 702-712.
- Lothenbach, B., K. Scrivener and R. D. Hooton (2011). "Supplementary cementitious materials." *Cement and Concrete Research* **41**(12): 1244-1256.
- Lura, P. (2003). Autogenous deformation and internal curing of concrete, TU Delft, Delft University of Technology.
- Lura, P., F. Durand and O. M. Jensen (2006). "Autogenous strain of cement pastes with superabsorbent polymers." International RILEM Conference on Volume Changes of Hardening Concrete: Testing and Mitigation: 57-65.
- Lura, P., O. M. Jensen and K. van Breugel (2003). "Autogenous shrinkage in high-performance cement paste: An evaluation of basic mechanisms." *Cement and Concrete Research* **33**(2): 223-232.
- Ma, X. W., J. H. Liu, Z. M. Wu and C. J. Shi (2017). "Effects of SAP on the properties and pore structure of high performance cement-based materials." *Construction and Building Materials* **131**: 476-484.
- Mechtcherine, V. and H.-W. Reinhardt (2012). Application of super absorbent polymers (SAP) in concrete construction: state-of-the-art report prepared by Technical Committee 225-SAP, Springer Science & Business Media.
- Philleo, R. E. (1991). "Concrete science and reality." *Materials science of concrete II*: 1-8.
- Shi, C., D. Wang, L. Wu and Z. Wu (2015). "The hydration and microstructure of ultra high-strength concrete with cement-silica fume-slag binder." *Cement and Concrete Composites* **61**: 44-52.
- Shi, C. J., Z. M. Wu, J. F. Xiao, D. H. Wang, Z. Y. Huang and Z. Fang (2015). "A review on ultra high performance concrete: Part I. Raw materials and mixture design." *Construction and Building Materials* **101**: 741-751.

- Snoeck, D., O. M. Jensen and N. De Belie (2015). "The influence of superabsorbent polymers on the autogenous shrinkage properties of cement pastes with supplementary cementitious materials." *Cement and Concrete Research* **74**: 59-67.
- Tuan, N. V., G. Ye and K. van Breugel (2010). "Internal Curing of Ultra High Performance Concrete by Using Rice Husk Ash." *International Rilem Conference on Material Science (Matsci), Vol Iii* **77**: 265-274.
- Wang, D. H., C. J. Shi, Z. M. Wu, J. F. Xiao, Z. Y. Huang and Z. Fang (2015). "A review on ultra high performance concrete: Part II. Hydration, microstructure and properties." *Construction and Building Materials* **96**: 368-377.
- Wu, L., N. Farzadnia, C. Shi, Z. Zhang and H. Wang (2017). "Autogenous shrinkage of high performance concrete: A review." *Construction and Building Materials* **149**: 62-75.
- Wu, Z. M., C. J. Shi, K. H. Khayat and S. Wan (2016). "Effects of different nanomaterials on hardening and performance of ultra-high strength concrete (UHSC)." *Cement & Concrete Composites* **70**: 24-34.
- Wyrzykowski, M., S. Ghourchian, S. Sinthupinyo, N. Chitvoranund, T. Chintana and P. Lura (2016). "Internal curing of high performance mortars with bottom ash." *Cement & Concrete Composites* **71**: 1-9.
- Zhutovsky, S. and K. Kovler (2017). "Influence of water to cement ratio on the efficiency of internal curing of high-performance concrete." *Construction and Building Materials* **144**: 311-316.