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Influence of ultra-fine fly ash on hydration shrinkage of cement paste①

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Abstract: Hydration shrinkage generated by cement hydration is the cause of autogenous shrinkage of high strength concrete. It may result in the volume change and even cracking of mortar and concrete. According to the data analysis in a series of experimental studies, the influence of ultra-fine fly ash on the hydration shrinkage of composite cementitious materials was investigated. It is found that ultra-fine fly ash can reduce the hydration shrinkage of cement paste effectively, and the more the ultra-fine fly ash, the less the hydration shrinkage. Compared with cement paste without the ultra-fine fly ash, the shrinkage ratio of cement paste reduces from 23.4% to 39.7% when the ultra-fine fly ash replaces cement from 20% to 50%. Moreover, the microscopic mechanism of the ultra-fine fly ash restraining the hydration shrinkage was also studied by scanning electron microscopy, X-ray diffraction and hydrated equations. The results show that the hydration shrinkage can be restrained to a certain degree because the ultra-fine fly ash does not participate in the hydration at the early stage and the secondary hydration products are different at the later stage.

Key words: ultra-fine fly ash; cement paste; hydration shrinkage; mechanism
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1 INTRODUCTION

Hydration shrinkage is also known as chemical shrinkage[1]. The solid volume increases after cement hydrating, but the absolute volume of cement water system reduces. Usually the total amount of volume shrinkage of cement water system is 7%-9%[1,2]. With the development of the technology of cement and concrete, concrete with high strength and high performance is the developing tendency now. However, nowadays, compared with ordinary concrete, the hydration shrinkage of high performance cement concrete increases obviously because of the acceleration of cement hydration. Meantime the hydration shrinkage is also the source of autogenous shrinkage of high strength concrete[3].

Due to the favorable activation effect, figuration effect and tiny aggregation effect in the process of cement hydration[4,5], ultra-fine fly ash (UFA) has already become the 5th fundamental component in producing high performance concrete. Sen et al [6,7] testified that when fly ash is equivalently added into cement paste, the fly ash will act as inertia stuffing and fill in the small apertures at the early stage. At the later stage, it will produce low-basicity C—S—H gel in the second-time hydration, and the intensity will continue to increase. The difference of the hydrating process and reactions between cement paste with fly ash and that without fly ash results in the difference of hydration shrinkage. In this paper, the influence of UFA on the hydration shrinkage of the high performance cement paste was studied. Then from the binding material hydrating mechanism, the reduction of the hydration shrinkage by adding UFA was analyzed.

2 EXPERIMENTAL

2.1 Materials

2.1.1 Cement

42.5 grade Portland cement, with the special surface area of 330 m^2/kg, density of 3.15 g/cm^3, was used. Its indexes of performance are shown in Table 1.

2.1.2 Ultra-fine fly ash

UFA was produced in Xiangtan Power Plant, Hunan. The density is 2.20 g/cm^3, the ignition loss is 3.2%, the water content ratio is less than 1%, and the specific surface area is 600 m^2/kg.

2.2 Devices and methods

So far no uniform method for measuring hydration shrinkage of cement paste has been developed[8,9]. According to the method introduced by Tazawa[10], a suit of device was designed, as shown in Fig. 1, and it reflects the volume change of the cement water system in terms of the descent height of the system surface.

The experimental processes are as follows.

1) The experimental materials were put into an open soft rubber bottle, an appropriate amount

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Table 1 Indexes of cement performance (ISO standard)

Cement variety	Fineness/%	Setting time/min		Strength(3 d)/MPa		Strength(28 d)/MPa	
		Initial set	Final set	Compression strength	Flexural strength	Compression strength	Flexural strength
42.5 grade Portland cement	3.3	284	384	32.8	6.0	60.9	8.9

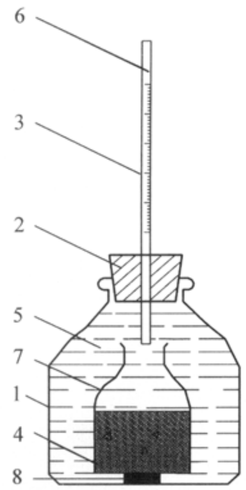

Fig. 1 Experimental device of hydration shrinkage

1—Jar; 2—Rubber cork perforated at center; 3—Burette; 4—Cement paste; 5—Water; 6—Surface covered by liquid paraffin; 7—Open soft rubber bottle; 8—Mat lump

of water was poured into the open soft rubber bottle, the sample was scattered and mixed with a glass stick to drain bubbles.

2) The open soft rubber bottle and cement paste were put into the jar. The mat lump was used to separate the soft rubber bottle from the bottom of the bottle.

3) The opening of the jar was stuffed up by the rubber cork, and the contact parts were sealed tightly by paraffin.

4) Water was dripped into the jar from a burette until the surface was close to the maximum scale.

5) A drop of liquid paraffin was dripped into the burette, covering the water surface to prevent water from vaporizing.

6) The device was placed in the standard curing room. The origin water surface was recorded after water surface was stabilized.

According to the result of the experiments, the hydration shrinkage value of cement water system could be measured, which is reflected by the descent of water surface in the burette.

3 RESULTS AND DISCUSSION

Design 5 groups of experiments to study the influence of UFA in cement paste. In every group 3 samples were tested, and the values of hydration shrinkage were recorded respectively at the ages of 1, 2, 3, 6, 12 h and 1, 3, 7, 14, 21, 28 d. The mean value was regarded as the final outcomes.

Because the maximum volume scale of the burette is 5 cm^3, each time 50 g sample was measured. The measuring outcomes of the 5 groups sample are shown in Fig. 2, where "C" stands for cement. In these samples, the first group was pure cement paste, the cements in the other 4 groups were replaced by UFA with the proportions (mass fraction) of 20%, 30%, 40% and 50%, respectively.

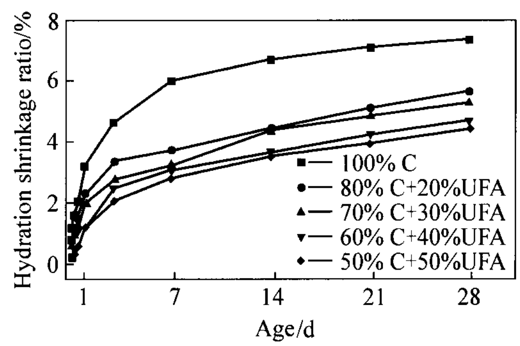

Fig. 2 Effect of amount of UFA on hydration shrinkage ratio of cement paste

According to Fig. 2, the more the UFA, the less the hydration shrinkage, especially at early age of hydration. For example, at about 7 d, the hydration shrinkages of the cement paste with 20%, 30%, 40% and 50% UFA in the paste, are respectively 61.7%, 53.3%, 51% and 46.7% of those of the cement paste without UFA. Until 28 d, these values are also much less than those of the ordinary cement paste.

Table 2 shows the change of the volume and density of cement paste before and after hydration. According to the calculation results, a fact should be noticed that the volume(mL) of hardened cement paste (HCP) increases and the density of HCP decreases with the increase of UFA (in 28 d), that is, V_5' (78.16) > V_4'(76.55) > V_3' (74.58) > V_2' (72.85) > V_1' (68.39) and ρ_1'(2.106)>ρ_2'(1.977)>ρ_3'(1.931)>ρ_4'(1.881) >ρ_5'(1.842). So the increased solid phase volume due to the increase of UFA can compensate for the hydration shrinkage.

Table 2 Change values of volume and density of solid phase of cement paste

Serial No.	m(FCP) /g			V(FCP)/mL				ρ(FCP)/ (g · cm⁻³)	V′ and ρ′(HCP) for 28 d	
	C	UFA	W	V_1(C)	V_1(UFA)	V_2(W)	V		V′/mL	ρ′/(g · cm⁻³)
1	100	0	44	31.75	0	44	75.75	1.901	68.39	2.106
2	80	20	44	25.40	9.09	44	78.49	1.835	72.85	1.977
3	70	30	44	22.22	13.64	44	79.86	1.803	74.58	1.931
4	60	40	44	19.05	18.18	44	81.23	1.773	76.55	1.881
5	50	50	44	15.87	22.73	44	82.60	1.743	78.16	1.842

Note: 1) FCP stands for fresh cement paste, HCP stands for hardened cement paste, C stands for cement, W stands for water; 2) *m* stands for total mass of FCP, *V* stands for total volume of FCP, V_1 stands for volume of solid, V_2 stands for volume of liquid, ρ stands for density of FCP, V' stands for total volume of HCP, ρ′stands for density of HCP; 3) It should be hypothesized that the cement is hydrated completely, thus the minimum water-cement ratio (*w/c*) is 0.44.

4 MECHANISM OF HYDRATION SHRINKAGE REDUCING BY ULTRA-FINE FLY ASH

4.1 Microscopic effect of ultra-fine fly ash

In order to analyze the effect of UFA in the process of cement hydration, scanning electron microscope tests were carried out for the UFA and the cement paste at different hydration ages (see Figs. 3 - 6). And X-ray diffraction analysis for ordinary cement paste and cement paste with UFA was performed. The results are shown in Fig. 7.

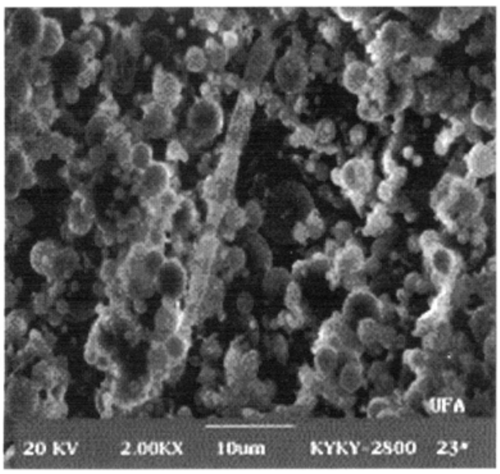

Fig. 3 SEM image of UFA

It can be seen from Fig. 3 that most UFA exists in the shape of ball, which can reduce the amount of water participating cement hydration. From Fig. 4, it can be seen that UFA almost does not take part in hydration at early age (7 d), and fill in the small apertures evenly with the tiny aggregated form. Fig. 5 demonstrates that UFA starts to hydrate partly at the age of 14 d. And at the period of 28 d, hydration products obviously appear on the surface of UFA (Fig. 6), which is attributed to the secondary hydration caused by pozzuolanic effect of UFA[11-14].

It is shown from Fig. 7 that the diffraction

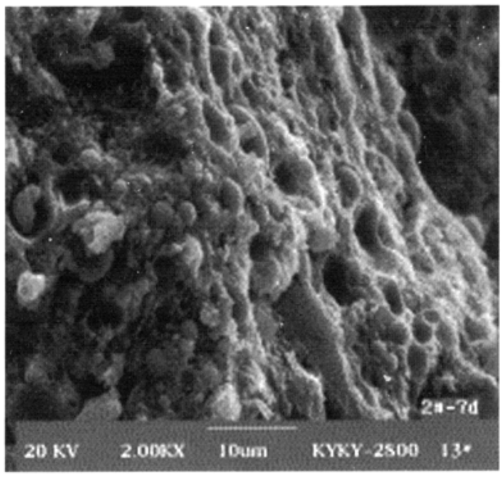

Fig. 4 SEM image of HCP containing UFA at age of 7 d

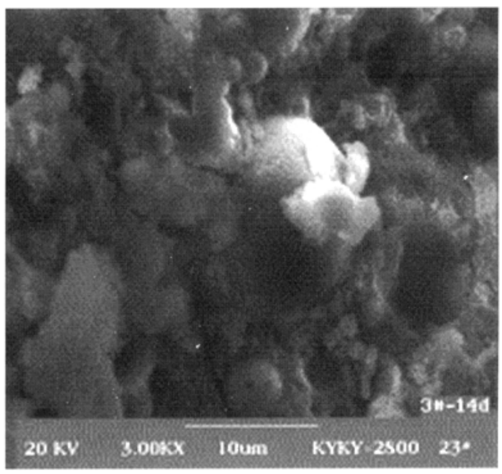

Fig. 5 SEM image of HCP containing UFA at age of 14 d

peaks of $Ca(OH)_2$ in cement paste with UFA are enhanced gradually before 14 d, but weakened gradually after 14 d. That is because UFA starts to join in the hydration and consumes some $Ca(OH)_2$. At the age of 60 d, the diffraction peaks of

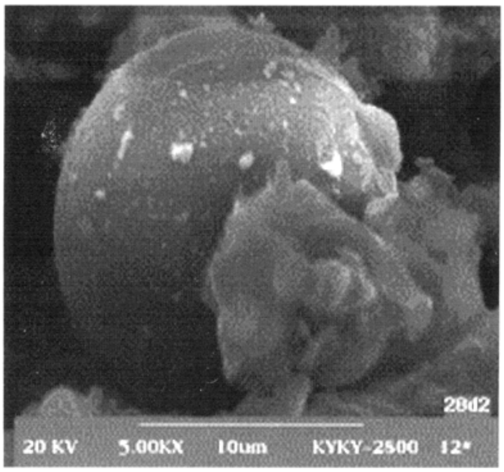

Fig. 6 SEM image of HCP containing UFA at age of 28 d

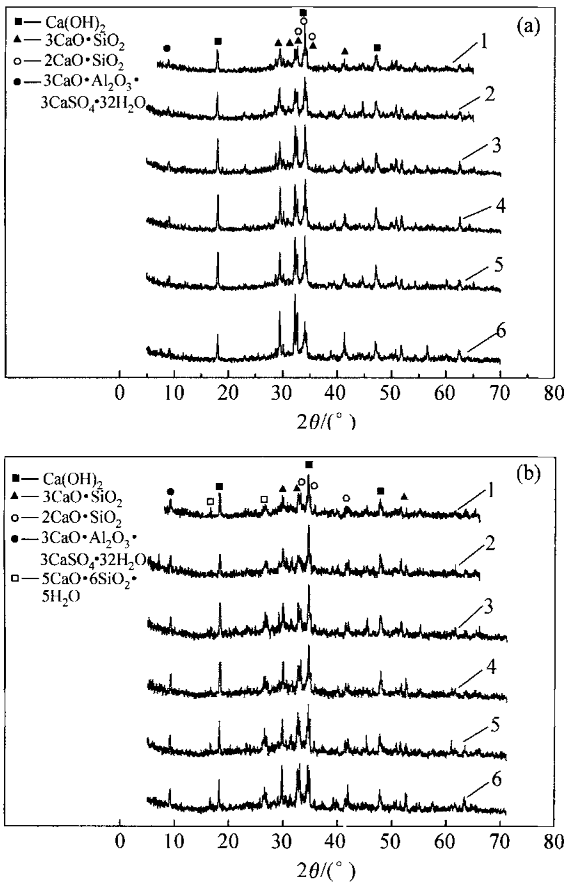

Fig. 7 XRD patterns of cement paste at different ages

(a)—Ordinary cement paste;
(b)—Cement paste containing UFA
Age/d: 1—60; 2—28; 3—14; 4—7; 5—3; 6—1

$Ca(OH)_2$ still exist, but the intensity of them is decreased obviously, which reflects that the amount of UFA participating in hydration is increased obviously.

To sum up, in the process of cement paste hydration, the effects of figuration and tiny aggregation of UFA are dominant at early age, at middle and late age the pozzuolanic effect of UFA acts gradually. However, the hydrating ability of UFA is low, and the amount of water participating in the process of UFA hydration can be less than that of pure cement, thus the total volume shrinkage is less than that of ordinary cement paste from macroscopic aspects.

4.2 Hydrated equations of hydration shrinkage of cement paste with ultra-fine fly ash

The influence of the addition of UFA on hydration shrinkage of cement paste was studied further from the aspect of hydration.

For pure cement paste, the hydration shrinkage caused by hydration can be calculated from hydration equations[11].

Take the hydration of $3CaO \cdot SiO_2$ for an example. The calculation of hydration shrinkage is shown in Table 3.

$$2(3CaO \cdot SiO_2)+6H_2O=$$
$$3\,CaO \cdot 2\,SiO_2 \cdot 3\,H_2O+3Ca(OH)_2$$

Table 3 Calculation of hydration shrinkage(Ⅰ)

	$2(3CaO \cdot SiO_2)$	$6H_2O$	$3\,CaO \cdot 2\,SiO_2 \cdot 3\,H_2O$	$3Ca(OH)_2$
Density	3.14	1.00	2.44	2.23
Molecular mass	228.23	18.02	342.48	74.10
Molar volume	72.71	18.02	140.40	33.23
Total volume	145.42	108.12	140.40	99.69

The volume shrinkage value is $V_L - V_R = (145.42 + 108.12) - (140.40 + 99.69) = 13.54$ cm^3, where V_L refers to the total volume before hydration, and V_R refers to the total volume after hydration.

The volume shrinkage ratio is $(V_L - V_R)/V_L = 0.0534 \times 100\% = 5.34\%$.

To analyze conveniently the hydration shrinkage of cement paste with UFA, the main activated component of UFA with SiO_2 (>50%) is considered.

The following are the hydrated equations of SiO_2 hydration[15]:

$$5\,Ca(OH)_2+6\,SiO_2+4\,H_2O=$$
$$5\,CaO \cdot 6SiO_2 \cdot 9\,H_2O$$

The Calculation of hydration shrinkage is shown in Table 4.

The volume shrinkage values is $(V_L - V_R) = (166.15+136.08+72.08)-369.58=4.73$ (cm^3). The volume shrinkage ratio is $(V_L - V_R)/V_L = 0.0126 \times 100\% = 1.26\%$.

Table 4 Calculation of hydration shrinkage(Ⅱ)

	$5Ca(OH)_2$	$6SiO_2$	$4H_2O$	$5CaO \cdot 6SiO_2 \cdot 9H_2O$
Density	2.23	2.65	1.00	2.20
Molecular mass	74.10	60.09	18.02	813.08
Molar volume	33.23	22.68	18.02	369.58
Total volume	166.15	136.08	72.08	369.58

In fact, it should be noticed that the final hydration product of fly ash-$Ca(OH)_2$ is C—S—H(Ⅰ). Its mole ratio of CaO the SiO_2 ratio is 0.8 - 1.5 and lower than that of the Portland cement product C—S—H(Ⅱ)(1.5 - 2.0). On the other hand, the density of C—S—H(Ⅰ) is 2.20 g/cm^3 and is less than that of C—S—H(Ⅱ) (2.44 g/cm^3). The structure of C—S—H(Ⅰ) is similar to that of natural Tobermorite (which is $C_5S_6H_9$ when water is sufficient)[15]. From the above calculation, it can be concluded that though the secondary hydration of UFA also causes the volume shrinkage, its volume shrinkage ratio is much less than that of pure cement, thus it can reduce the total hydration shrinkage ratio. Meantime, the density of C—S—H produced by hydration of cement paste with UFA is less than that of ordinary cement paste, and hence its amount is more than hydration products of ordinary cement paste, which means the same amount of cement with UFA produces more solid phase volume compared to pure cement, thus it can reduce the hydration shrinkage caused by different mean densities before and after reaction.

5 CONCLUSIONS

1) Hydration shrinkage of cement paste can be restrained by the addition of UFA. The more the UFA is added, the less hydration shrinkage.

2) The microscopic effects of UFA, such as tiny aggregation, pozzuolanition, are the reasons for UFA reducing hydration shrinkage.

3) It is proved that the secondary hydration of UFA can reduce the hydration shrinkage effectively from the aspects of cementitious materials hydration equations and hydration products.

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