

# Hydration mechanism of low quality fly ash in cement-based materials

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**Abstract:** The hydration mechanism of low quality fly ash in cement-based materials was investigated. The hydration heat of the composite cementitious materials was determined by isothermal calorimetry, and the hydration products, quantity, pore structure and morphology were measured by X-ray diffraction (XRD), thermogravimetry-differential thermal analysis (TG-DTA), mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM), respectively. The results indicate that grinding could not only improve the physical properties of the low quality fly ash on particle effect, but also improve hydration properties of the cementitious system from various aspects compared with raw low quality fly ash (RLFA). At the early stage of hydration, the low quality fly ash acts as almost inert material; but then at the later stage, high chemical activity, especially for ground low quality fly ash (GLFA), could be observed. It can accelerate the formation of hydration products containing more chemical bonded water, resulting in higher degree of cement hydration, thus denser microstructure and more reasonable pore size distribution, but the hydration heat in total is reduced. It can also delay the induction period, but the accelerating period is shortened and there is little influence on the second exothermic peak.

**Key words:** low quality fly ash; cement-based materials; hydration products; pore structure

## 1 Introduction

Fly ash is a by-product of coal combustion and abundantly available in China [1–2]. Statistical data [3] showed that just in the year of 2000, up to  $3 \times 10^8$  ton of fly ash was consumed, accounting for 60% of the total emission. But still a large amount of fly ash has not been recycled and the quantity is on the rise. At present, China is falling behind some developed countries in the utilization of fly ash such as Germany and Switzerland [4]. So, in new proposed “Twelfth Five-year” plan by the government, it is aimed to increase the comprehensive utilization rate of fly ash up to 70% in 2015 and the recycling capacity by  $6 \times 10^7$  ton per year.

Another form of ash which is produced directly falling into the bottom of the boiler, called furnace slag also low quality fly ash, can not meet the requirement of the secondary fly ash. An extremely large number of the low quality fly ash cause severe environmental pollution since it is rarely used. By contrast, high quality fly ash is widely used as an mineral admixture in concrete [5–7]. Because of the wide applications, a great variety of work has been done on this kind of fly ash previously,

involving physical and chemical activities [8–9], activity stimulation [10–11], effect mechanism [12] in cement-based materials.

On the other hand, in order to improve the utilization rate of low quality fly ash, more in-depth researches for low quality fly ash must be done. But the research data for low quality fly ash are very limited and many problems remain to be solved. For example, it is still unknown whether low quality fly ash has the same activity stimulation and hydration mechanism as normal fly ash, especially how to calculate the contribution proportion of the physical and chemical activity in the hydration process of cement-based materials. Based on our previous studies, concrete containing low quality fly ash can achieve high strength and durability [13]. But the hydration mechanism is not been well understood yet. Therefore, some mechanism researches will be dealt with in this work and taken grinding technology to improve its hydration properties.

## 2 Experimental

### 2.1 Raw materials

Ordinary Portland cement (OPC) P.O 42.5 is supplied

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by Huaxin Cement Plant whose performance parameters meet the requirements in the Standard GB 175—2007, and low quality fly ash (FA) is supplied by Guanyinyan Hydropower Project. Chemical compositions of the cement and fly ash determined by X-ray fluorescence (XRF) are listed in Table 1.

**Table 1** Main chemical composition (mass fraction) of cement and low quality fly ash (%)

Sample	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
OPC	23.61	3.44	4.06	59.59	2.51
LFA	53.41	4.28	25.79	2.60	2.79
Sample	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	LOI	
OPC	0.86	0.19	-	3.00	
LFA	1.38	0.42	0.30	3.67	

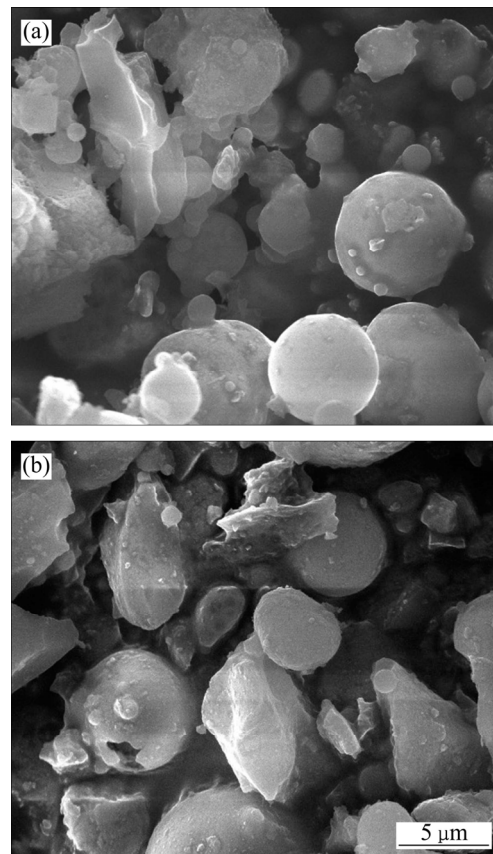
**2.2 Grinding of LFA**

For economic reasons, the low quality fly ash was ground in a testing mill for 45 min, and the fineness and water requirement could be controlled and close to the limits of the secondary fly ash in Chinese Standard DL/T 5055–2007 (Table 2). Raw low quality fly ash (RLFA) is mainly made of big porous vitreous (Fig. 1(a)), with a few glass beads scattered. After being ground, fewer glass beads but more small porous vitreous could be seen in ground low quality fly ash (GLFA) (Fig. 1(b)). Further analysis of physical properties and particle size showed, obviously, that the fineness of GLFA is improved, specific surface nearly tripled and more fine particles appeared. Compared with beads, the porous vitreous can improve the specific area by broken polyhedrons after ground. That explains why the specific area of GLFA is as high as 794 m<sup>2</sup>/kg, but that of RLFA is 278 m<sup>2</sup>/kg (Table 2). Additionally, besides the coarse particles, the major porous vitreous in low quality fly ash contains much mullite and α-quartz which have negative effect on its pozzolanic activity. So, the crystal structure of fly ash can be changed by grinding to increase the activity of silicon aluminium group. The particle size analysis of three materials was carried out by OMEC LS-C (III) laser particle sizer and the particle size distribution is listed in Table 3.

**Table 2** Physical properties of OPC, RLFA and GLFA

Sample	Residue on sieve of 45 μm/%	Water requirement/%	Specific area/(m <sup>2</sup> ·kg <sup>-1</sup> )
OPC	—	—	437
RLFA	49.8	99.6	278
GLFA	19.7	100.4	794
Control	≤25	≤105	—

Note: Control is the limits of secondary fly ash in DL/T 5055—2007.



**Fig. 1** SEM images of RLFA and GLFA: (a) RLFA; (b) GLFA

**Table 3** Particle size distributions of OPC, RLFA and GLFA

Sample	Cumulative percentage/%			Characteristic of particle size/μm		
	≤10 μm	≥30 μm	≥45 μm	D10	D50	D90
OPC	41.33	16.22	1.6	2.37	13.6	40.36
RLFA	16.35	61.58	48.93	5.86	52.14	144.54
GLFA	44.87	29.00	19.70	1.39	12.42	64.05

**2.3 Testing methods**

The same cement replacement ratios (20%, 40% and 60%) of RLFA (group R) and GLFA (group G) were used to analyze their effect mechanism on the hydration properties of cement-based materials compared with the pure cement control sample (Table 4). Mix proportions of pastes are listed in Table 4. 40 mm×40 mm×40 mm cubic paste specimens of group R and group G with water to cementitious materials ratio (W/C) of 0.4 were prepared and tested at curing age of 3, 7, 28 and 90 d.

OPC, R2, R4, G2 and G4 were selected to measure the hydration heat by TAM isothermal calorimeter. W/C was 0.4, cementitious material dosage was 10 g with an accuracy of 0.001 g. Hydration reaction was carried out in 20 mL of ampere bottle and the temperature is 20 °C.

The cement pastes were prepared in a paste mixer according to EN 196-3 and cured at 23 °C till testing age. Microstructure of the samples was measured by means of

**Table 4** Mix proportions of pastes

Sample	Cement	GLFA	RLFA	Water
OPC	1.00	–	–	0.40
R2	0.80	–	0.20	0.40
R4	0.60	–	0.40	0.40
R6	0.40	–	0.60	0.40
G2	0.80	0.20	–	0.40
G4	0.60	0.40	–	0.40
G6	0.40	0.60	–	0.40

XRD, TG-DTA, and SEM techniques. X-ray diffraction analyzer is D/MAX-RB models of target X-ray diffraction, using copper target and continuous scan, produced by RIGAKU. TG-DTA in an N<sub>2</sub>-atmosphere up to a temperature of 1200 °C adopted the Diamond TG/DTA analyzer, produced by Perkin Elmer Instruments Plant. Mercury Injection Apparatus is Auto Pore IV (9500), the pressure ranges from 0.20 to 60000.00 psi (about 413.76 MPa to 1.38 kPa), and calculation of measuring pore size range is about 30Å–0.9 mm.

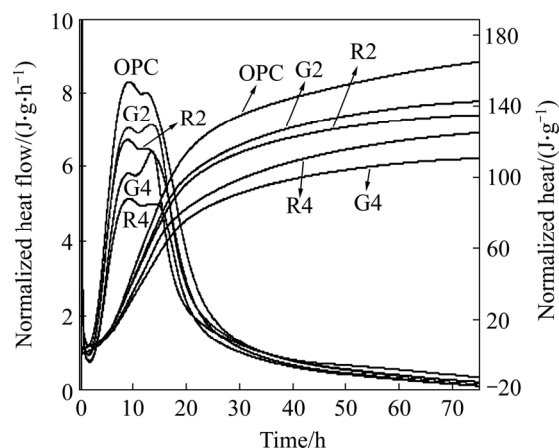
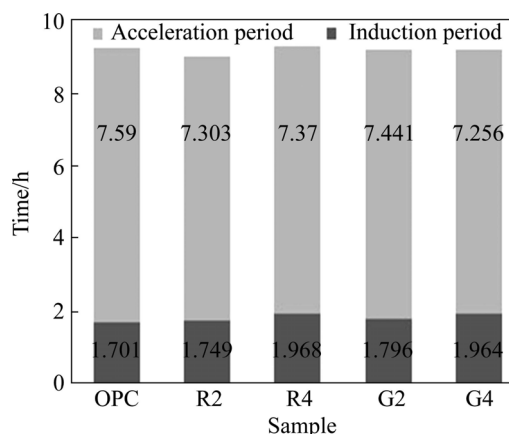
### 3 Results and discussion

#### 3.1 Hydration process

The development of hydration heat and rate of group R, group G and OPC sample at 20 °C are shown in Fig. 2. The addition of RLFA or GLFA has little difference on the five stages of hydration with OPC. But RLFA and GLFA did reduce the hydration rate and total heat compared to the OPC. It is clear that every composite system as well as the OPC has the third exothermic peak, which caused by the convert of Aft to AFm as the result of the consumption of gypsum. The third exothermic peak of the GLFA system is much higher than its second exothermic peak, but it is inverted for the RLFA system, and every third exothermic peak is weaker than its second exothermic peak. These indicated fine-grinding led to hydration reaction more quickly, RLFA and GLFA as mineral admixtures reduced hydration heat which is beneficial to mass concrete construction.

Figure 3 shows induction period and acceleration period in hydration process [8, 13]. From Fig. 2 and Fig. 3, in the OPC sample and the composite systems, the induction period started at about 1 h, but ended at different time. The addition of fly ash prolonged the induction period, but shortened the acceleration period obviously compared with OPC, which identified that fly ash has little effect on the appearance of second exothermic peak. At early hydration period, fly ash was considered to be inert material, but to be pozzolanic material at the later period and present chemical activity.

With the hydration of cement particles at the first few minutes, both the effective water and hydration heat increased. With the increase of RLFA content, the acceleration period prolonged as well as the induction period. But as for GLFA system, the acceleration period and the induction period will be shortened. There are two reasons for the extension of induction period. On one hand, the increase of the effective water reduced the Ca<sup>2+</sup> concentration in pore solution, extending the induction period by increasing the time for Ca<sup>2+</sup> saturation; on the other hand, GLFA sphere particles could adsorb Ca<sup>2+</sup> in the solution, inhibit the increasing of Ca<sup>2+</sup> concentration through adsorption in the first few hours and delay the portlandite (CH) and calcium silicate hydrate (C—S—H) crystallization nucleation, thus resulting in a delay of cement hydration. In the accelerated phase, more water could contact with the exposed new surface to accelerate the cement hydration because of the increase of effective water. In short, the nucleation effect of GLFA can also accelerate the cement hydration.

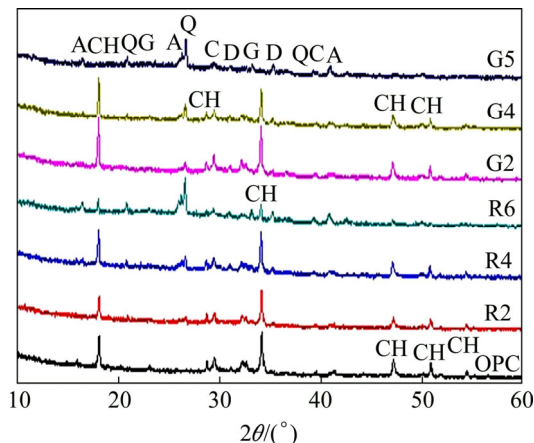
**Fig. 2** Hydration heat and rate normalized of samples**Fig. 3** Induction period and acceleration period of samples

#### 3.2 Microstructure

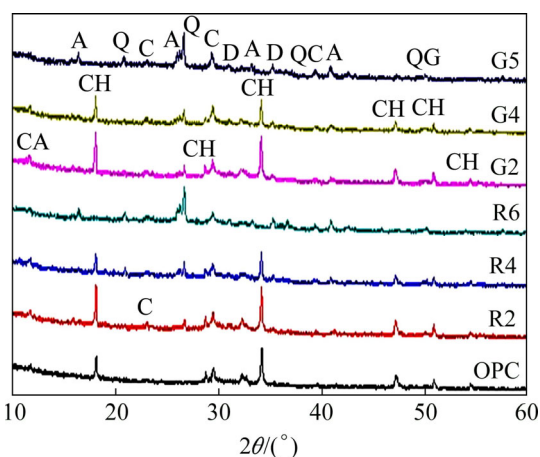
##### 3.2.1 Hydration products and hydration degree

Details of the measured XRD patterns are shown in Figs. 4 and 5. The identified crystalline phases are

portlandite, calcite, quartz and gypsum. From these figures, the types of hydration products of the group R and group G are portlandite, calcite, quartz, gypsum and dolomite, while only portlandite and calcite crystals appeared in OPC sample.



**Fig. 4** XRD patterns of samples at 7 d (CH–Portlandite; C–Calcite; Q–Quartz; G–Gypsum; D–Dolomite; A–Calcium aluminum oxide)

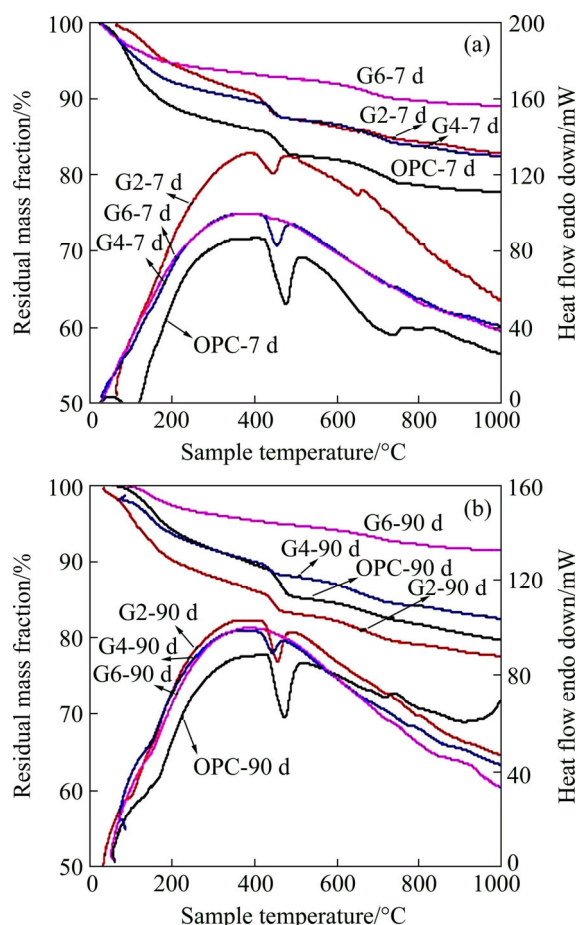


**Fig. 5** XRD patterns of samples at 90 d (CH–Portlandite; C–Calcite; Q–Quartz; G–Gypsum; D–Dolomite; A–Calcium aluminum oxide)

With the increase of RLFA or GLFA contents, the characteristic peak of hydration production portlandite (CH) weakened while the characteristic peak of dolomite and quartz enhanced. As for the same contents of RLFA and GLFA, grinding could stimulate the activity, which made the consumption quantity of CH at secondary hydration much higher, causing CH content at 90 d far less than that in 7 d. In addition, due to the consumption of cement clinker with hydration process, the characteristic peak of clinker was also reduced. When the content of fly ash reached higher than 40%, the CH reduced greatly and almost depleted at 90 d. This indicated exactly that fly ash presented filling effect in the early stage and showed pozzonlanic activity at later. The result lay on two aspects: one was that the CH

content decreased as the relative decrease of cement content; the other was that pozzonlanic activity became more obvious as admixture content increased at later stage. As for the content of 60%, CH crystal was almost disappeared, which indicated that CH production could not meet the needs of the pozzonlanic reaction.

The chemical bonded water content mainly depended on the quantity of hydration products, which was related to hydration degree. Based on Refs. [15–16], the calculation of chemical bonded water content can be calculated from Figs. 6 and 7, which can be adopted to calculate the degree of cement hydration and the results are also listed in Table 5 [17].



**Fig. 6** TG-DTA curves of OPC, G2, G4 and G6: (a) 7 d; (b) 90 d

Table 5 shows that chemical bonded water content decreased with the increase of fly ash content. No matter at 7 or 90 d, the higher the fly ash content, the less the quantity of chemical bonded water. At 7 d, the chemical bonded water content of group G was slightly higher than that of group R, and the difference enlarged at 90 d. At 7 d, as for the contents of 20% and 40%, the hydration degree of composite system was higher than that of pure cement sample, and the cement hydration was promoted at different levels. When the content increased up to 60%, the hydration degree was lower than that of OPC, which might be caused by over

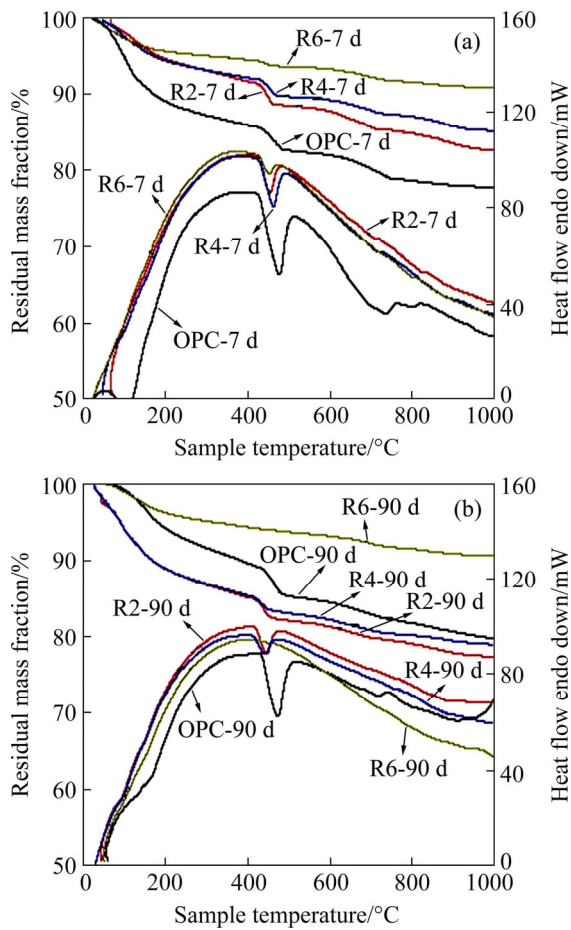


Fig. 7 TG-DTA curves of OPC, R2, R4 and R6: (a) 7 d; (b) 90 d

Table 5 Chemical bonded water content and hydration degree (%)

Sample	Chemical bonded water		Degree of hydration	
	7 d	90 d	7 d	90 d
OPC	13.88	16.62	13.88	16.62
R2	12.34	13.35	15.43	16.69
R4	9.33	11.53	15.55	19.22
R6	3.35	4.83	8.37	12.08
G2	12.91	14.89	16.14	18.62
G4	10.38	12.14	17.29	20.23
G6	5.23	6.89	13.07	17.23

dilution of cement clinker. Generally, fly ash can decrease the quantity of chemical bonded water at different levels, but improve the hydration degree even with a content up to 40%.

3.2.2 Pore microstructure

The MIP results of group G and OPC sample are shown in Fig. 8. As for the GLFA content of 20%, the total porosity decreased over time. This was due to the generation of hydration products in pores. At the same curing age of 90 d, the total porosity of G4 is lower than that of G2, which is easy to be understood that the

hydration products' quantity of G4 is less than that of G2. This conclusion just agreed with the results of the chemical bonded water calculation.

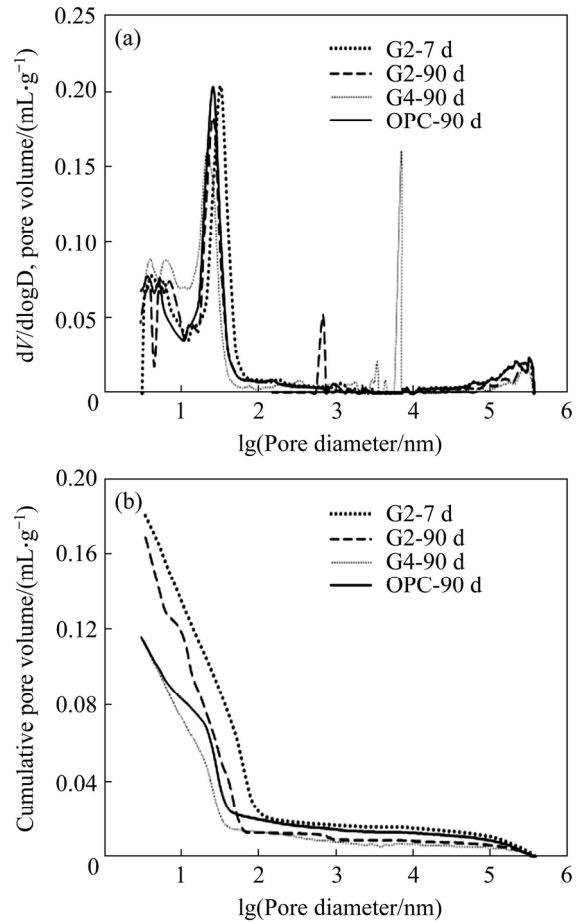


Fig. 8 Pore structure differential distribution and cumulative pore volume of samples

Table 6 shows the characteristic apertures in MIP analyses, including threshold aperture, most probable aperture, the average pore diameter, the size of pore diameter and pore diameter in the area. When GLFA content was 20%, the threshold aperture reached the highest value of 102 nm at 7 d, almost equal to the value of OPC. With the increase of GLFA content and curing age, the threshold aperture declined. At the later hydration stage, GLFA involved in the secondary hydration so as to reduce the macropore volume and make the threshold aperture lower. The most probable

Table 6 Characteristic aperture(nm)

Sample	Median pore diameter		Average pore diameter	Threshold aperture	Most probable aperture
	Volume	Area			
G2-7 d	28.4	6.4	14.0	102	32.4
G2-90 d	20.1	6.2	12.2	80	26.3
G4-90 d	16.7	5.9	10.5	40	21.1
OPC-90 d	43.9	5.8	16.1	100	26.3

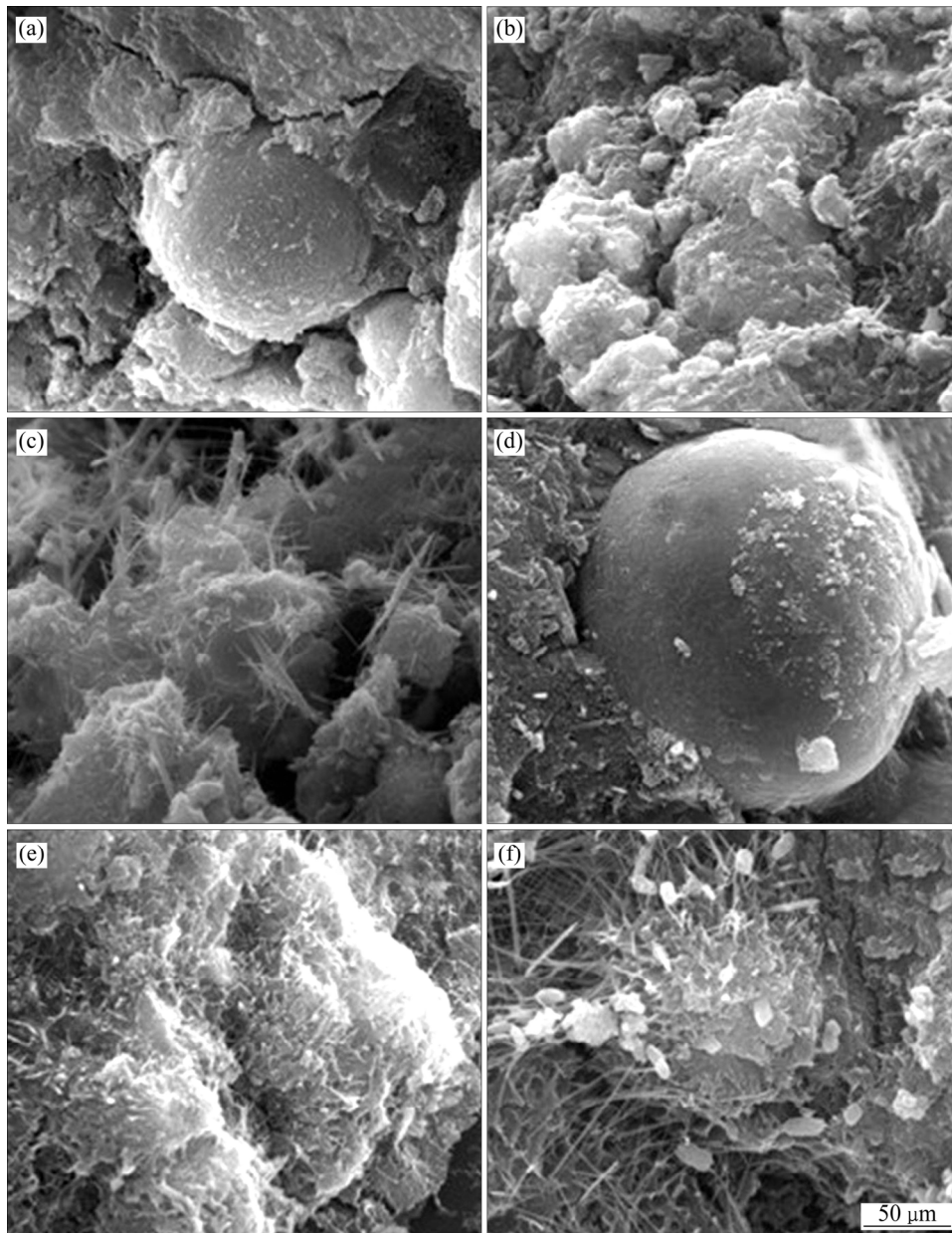
aperture size reflects the distribution of pore diameter. The higher the threshold aperture and the most probable aperture, the larger the average pore diameter. At 90 d, the most probable aperture of G2 was similar to that of OPC, around 26.3 nm, while at 7 d, the value of G2 was 32.4 nm. Paste containing GLFA reduced the most probable aperture, and made it more sensitive over curing age.

3.2.3 Morphology of hydration products

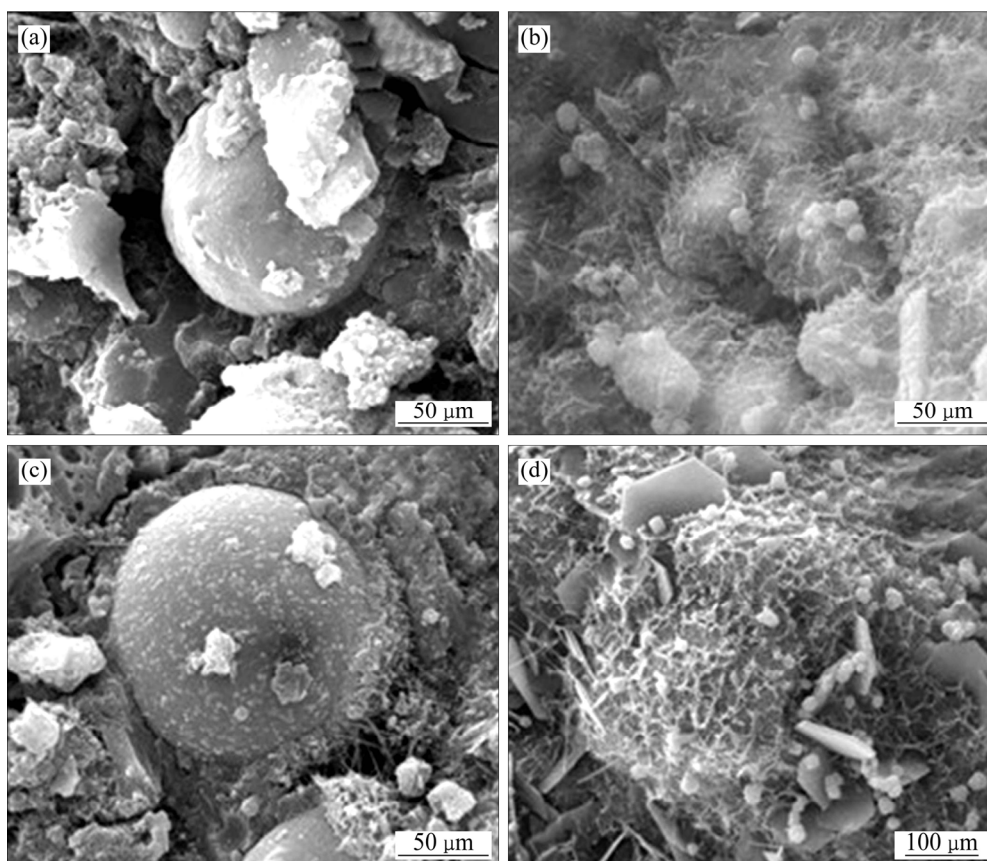
Fly ash particle could be observed clearly in Fig. 9, but the particle size of G2 is smaller than that of R2 due to grinding. Some C—S—H gel could be found around the particles, but there was no obvious reaction on fly ash particles surface at 28 d [18–19]. This indicated that fly ash acted as inert materials in early hydration. At 90 d,

some hydration products such as mesh C—S—H gel could be observed. Fly ash expressed its chemical activity at later stage, especially after being ground. Hence, the microstructure of G2 is denser than that of R2. When the fly ash content was 40%, some bar C—S—H gel formed. But the fly ash content could not be excessive, which would dilute the cement and reduce the hydration degree, as listed in Table 5.

Figure 10 shows the morphology of hydration products of samples containing 60% fly ash, in which spherical fly ash particles could be found and be surrounded by some other hydrates, such as C—S—H gel [20]. At 90 d, some layered CH could be found from R6, but it didn't appear in G6 which was attributed to the secondary hydration reaction of fine fly ash particles to



**Fig. 9** Morphology of hydration products of G2, G4, R2 and R4: (a) G2-28 d; (b) G2-90 d; (c) G4-90 d; (d) R2-28 d; (e) R2-90 d; (f) R4-90 d;



**Fig. 10** Morphology of hydration products of G6 and R6: (a) G6-28 d; (b) G6-90 d; (c) R6-28 d; (D) R6-90 d

consume up CH. The surface of fly ash particles in G6 and R6 was eroded, which reflected the fact that fly ash has participated in hydration reaction, although the quantity is limited [21–22]. Lots of hydration products interweaved each other and thus the hydration properties improved.

#### 4 Conclusions

Grinding not only affects physical properties but also improves the hydration of fly ash in cement-based materials. Compared with the control OPC sample and group R, GLFA can improve its hydration properties of cementitious system from different aspects. At the early age, the low quantity fly ash acts as almost inert material; but at the later stage, it appears high chemical activity, especially after being ground. It can also accelerate the generation of hydration products with more chemical bonded water, leading to higher hydration degree, denser microstructure and more reasonable pore size distribution.

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