

# Improvement of surface cementitious properties of coarse fly ash by dehydration and rehydration processes

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**Abstract** Owing to poor bonding between coarse fly ash particles and hydration products, gap-graded blended cements with fly ash usually show lower compressive strengths than Portland cement. Surface cementitious properties of coarse fly ash were improved by dehydration and rehydration processes in the present study. The results show that during the calcination at 750 °C, C–S–H gel is mainly transformed into a new nesosilicate, which is similar to a less crystalline C<sub>2</sub>S. The formation of melilite from hydration products is also noticed at 900 °C, however, this will not contribute to rehydration of calcined fly ash. Rehydration of new generated nesosilicate on the surface of coarse fly ash leads to a better bonding between coarse fly ash particles and hydration products. As a result, both early and late mechanical properties of gap-graded blended cements containing 25% cement clinker and 39% calcined coarse fly ash are higher than those of 100% Portland cements.

**Keywords** Fly ash · Dehydration · Rehydration · Blended cement · Compressive strength

## Introduction

Over 50% of the 3.3 billion tonnes of coal, annually produced in China, are used for power generation, which results in the generation of over 0.4 billion tonnes of fly ash [1]. Only about 30% of produced fly ash, mainly Class C or

F fly ash as specified in ASTM C 618 [2], is reused as a supplementary cementitious material (SCM) in blended cement producing or as a mineral admixture in concrete mixing. The rest can not be used in cement and concrete because of their coarse particle size or high carbon content.

In the previous study [3], high performance blended cements with low clinker content can be prepared through a gap-graded particle size distribution (PSD) and arranging cementitious materials in the PSD according to their hydraulic activities [4]. It is proved that fine SCMs fractions present higher strength contribution ratios than corresponding clinker fractions [5]. Cement clinker particles in the range of 8–24 μm are found to have superior properties in terms of low water requirement and high strength contribution [6]. Coarse clinker fractions are suggested to be replaced by low activity SCMs or perhaps inert fillers as this fraction mainly plays “filler effect” and makes little contribution to the strength development of blended cements [7].

Coarse fly ash is anticipated to be used in the coarse fractions of gap-graded blended cements. However, due to low pozzolanic activity, coarse fly ash particles always remain un-hydrated in blended cement paste, especially in early ages [8], which leads to fairly poor bonding between fly ash particles and hydration products. As a result, the compressive strengths of gap-graded blended cements with coarse fly ash (BCF) are much lower than those of 100% Portland cement [3]. C. Alonso proved that after calcination at 750 °C, C–S–H gel transforms into a nesosilicate form with a C<sub>2</sub>S stoichiometry close to larnite, but less crystalline, and rehydration of the new generated nesosilicate is observed when dehydrated hydration products contact with water [9–12]. With such a possibility, surface cementitious properties of coarse fly ash were improved by dehydration and rehydration processes, meanwhile the un-burnt carbon is ignited during the calcination. It is expected

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that compressive strengths of gap-graded BCF can be improved significantly due to a better bonding between coarse fly ash particles and hydration products. This method will contribute to the utilization of coarse fly ash as a SCM in cement and concrete producing. It is also a means of reducing CO<sub>2</sub> emissions and obtaining substantial energy and cost savings, by substituting coarse cement clinker with coarse fly ash.

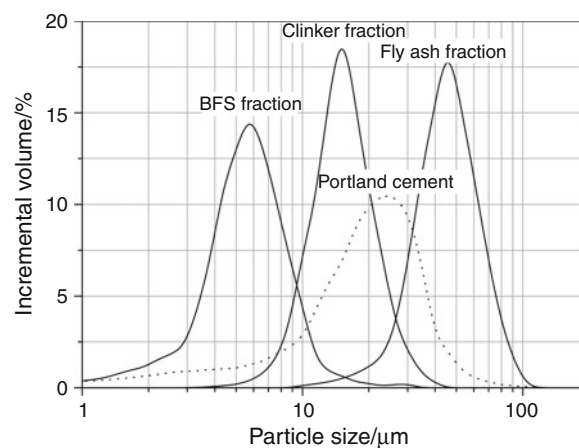
## Raw materials

Coarse fly ash fraction used in this experiment was obtained by classifying local available fly ash, which is collected from Zhujiang coal fire power plant. Chemical compositions of coarse fly ash fraction, middle clinker fraction, fine blast furnace slag (BFS) fraction, and an ASTM type I Portland cement determined by X-ray fluorescence spectroscopy (XRF) method are listed in Table 1. Middle clinker fraction and fine BFS fraction will be employed to produce gap-graded blended cements in “Gap-graded blended cements with calcined fly ash” section. It should be noted that the fly ash is a low calcium fly ash with high content of un-burnt carbon, which also has a very low Blaine fineness.

PSDs of raw materials, as measured by laser diffraction (Malvern Mastersizer 2000, refractive index of solid particle: 1.68, refractive index of dispersant (ethyl alcohol): 1.32 and obscuration: 12.4%), are shown in Fig. 1 and Table 2. From this, it can be seen that all fractions prepared have a narrow PSD and that the mean size of each fraction is nominally consistent with that of each filling grade of gap-graded PSD, which are 6, 16, and 45 μm, respectively [3]. In contrast, the Portland cement used shows a relatively wide PSD.

## Dehydration and rehydration processes of coarse fly ash

90% coarse fly ash and 10% lime are blended with water into a paste at a solid to solution ratio of 1.0, the paste was sealed and cured for 1, 3, 7, 10, 14, and 21 days at 20 ± 1 °C, and then vacuum-oven-dried at 65 °C for at



**Fig. 1** PSD of fly ash, BFS, clinker fractions, and Portland cement used in the experiment

least 48 h. The dried samples were calcined in a furnace at a heating rate of 10 °C/min. When the desired temperatures (650, 700, 750, 800, 850, or 900 °C) were reached, the samples were kept 2 h in the furnace at the desired temperature to allow the respective transformation to occur. The calcined samples were quickly cooled to room temperature after taking out from the furnace, and then characterized by X-ray diffraction (XRD, Cu K $\alpha$ 1, 40 kV and 40 mA), scanning electron microscopy (SEM, NanoSEM 430, 15 kV), and X-ray energy dispersive spectroscopy (EDS, Oxford 7573, 20 kV).

## Mineral phase changes during calcination

XRD patterns of calcined fly ash samples (pre-hydrated for 3 days) are shown in Fig. 2. Owing to low hydration degree of fly ash, mullite and quartz are still existed in fly ash after calcination at different temperatures. A significant peak, corresponding to CaCO<sub>3</sub>, is observed after calcination at 600 °C, and this peak gradually disappeared at elevated temperatures. It is proved that C–S–H gel transformed into a new nesosilicate, similar to a less crystalline C<sub>2</sub>S, during the calcination at 750 °C [9, 10]. However, the nesosilicate is not identified clearly by XRD in this experiment as only small amount of nesosilicate with less

**Table 1** Chemical compositions of raw materials employed in the experiment

Material	Chemical composition/%										Blaine fineness/ m <sup>2</sup> kg <sup>-1</sup>	Specific density/ kg m <sup>-3</sup>
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	LOI			
Coarse fly ash fraction	45.43	24.36	9.70	5.23	1.46	0.23	0.36	1.03	8.88	197	2.59	
Portland cement	21.60	4.35	2.95	63.81	1.76	0.51	0.16	2.06	1.19	345	3.15	
Middle clinker fraction	21.56	4.45	2.85	64.91	1.80	0.78	0.21	0.51	1.59	413	3.14	
Fine BFS fraction	35.72	12.26	0.26	36.56	11.28	0.48	0.25	1.21	-0.77	624	2.91	

Note: LOI loss on ignition

**Table 2** Parameters of PSD of raw materials employed in the experiment

Fraction	Fine BFS fraction	Middle clinker fraction	Coarse fly ash fraction	Portland cement
D <sub>10</sub> /μm	2.63	9.28	28.33	4.72
D <sub>50</sub> /μm	5.21	15.08	44.21	18.44
D <sub>90</sub> /μm	8.47	21.54	75.46	33.03

Note: D<sub>10</sub>, D<sub>50</sub>, and D<sub>90</sub> are the maximum particle diameters when cumulative volume reaches 10, 50, and 90%, respectively

crystallinity is generated on the surface of fly ash particles. At 900 °C, a diffraction peak of melilite is noticed, indicating that hydration products mainly transformed into melilite. It can be inferred that the surface cementitious properties will not be improved as melilite presents nearly no cementitious activity under normal conditions [13, 14].

Heat evolution curves of pastes made at a water-to-calcined fly ash (pre-hydrated for 3 days) mass ratio of 0.5 were followed for 72 h at 25 °C using a TAM-Air isothermal calorimeter according to ASTM C 1702-09 [15]. Figure 3 depicts that original fly ash show a slight heat of hydration. In contrast, heat of hydration of calcined fly ash is increased remarkably. Fly ash sample calcined at 750 °C presents the highest heat of hydration because of the rehydration of new generated nesosilicate and lime. Heat evolution curves of fly ash samples calcined at 900 and 600 °C show similar shape, but fly ash samples calcined at 900 °C presents a relatively higher heat of hydration due to larger amount of lime (caused by decomposition of CaCO<sub>3</sub>). It can be deduced that only hydration of lime happened and melilite remained un-hydrated in the fly ash sample calcined at 900 °C [16].

Dehydration and rehydration processes

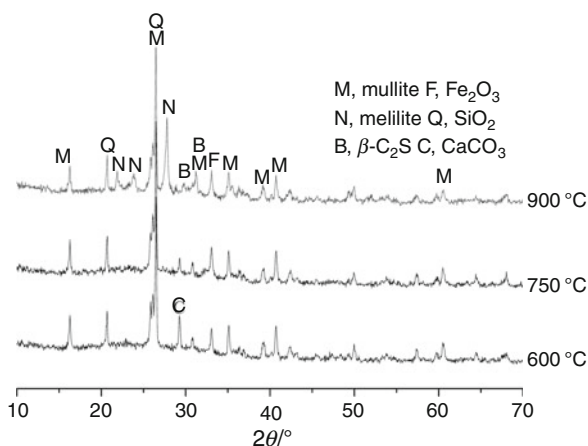
Figure 4a shows that original fly ash consists of both the spherical and irregular particles with high porosity, all of which have smooth surface. Figure 4b shows that after

calcination, fly ash particles appeared to be covered by a layer of smaller particles, which leads to a rough surface of fly ash particles. SEM image of calcined fly ash after being cured in water for 3 days is given in Fig. 4c, small amount of rehydration products is observed, by which surface cementitious properties of fly ash are expected to be improved. EDX results in Table 3 show that Ca content of point 3 and 4 on the surface of calcined fly ash is much higher than that of point 1 and 2 on the surface of original fly ash, implying a higher content of Ca in nesosilicate than in original fly ash. The rehydration products (point 5) are confirmed to be similar to normal C–S–H(I) gel, with a Ca/Si ratio of 1.0.

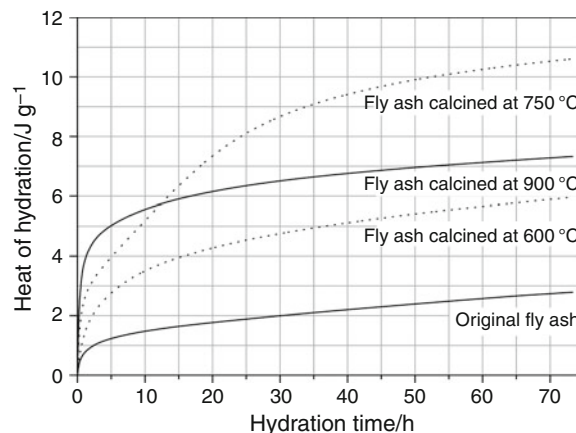
Activity index

Binders composed of 30% fly ash and 70% Portland cement by mass were prepared. Cement mortars were mixed at water:obtained binder:standard sand = 0.5:1:3 by mass and cast into 40 × 40 × 160 mm molds. After being cured at 20 ± 1 °C and relative humidity (RH) of 90% for 24 h, the specimens were demolded and cured in lime-saturated water at 20 ± 1 °C, followed by the strength tests according to EN 196-1 [17]. Activity index of the fly ash used was calculated as the strength ratio of the binders to Portland cement.

To investigate the influence of calcination temperature on activity index of calcined fly ash, fly ash samples were

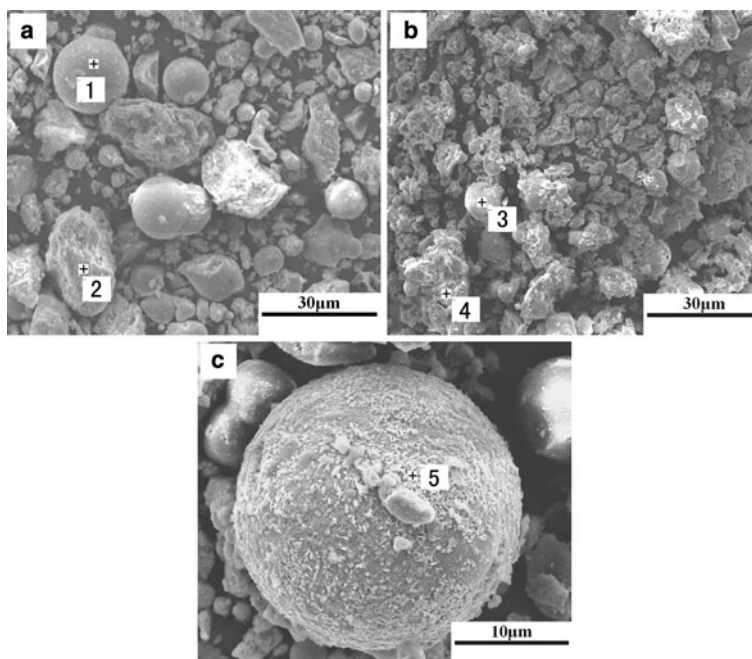


**Fig. 2** X-ray diffraction patterns of fly ash samples calcined at different temperatures



**Fig. 3** Heat evolution of fly ash samples calcined at different temperatures

**Fig. 4** SEM images of fly ash before and after calcination. **a** Original fly ash; **b** fly ash sample pre-hydrated for 3 days and calcined at 750 °C; **c** rehydration of fly ash sample calcined at 750 °C

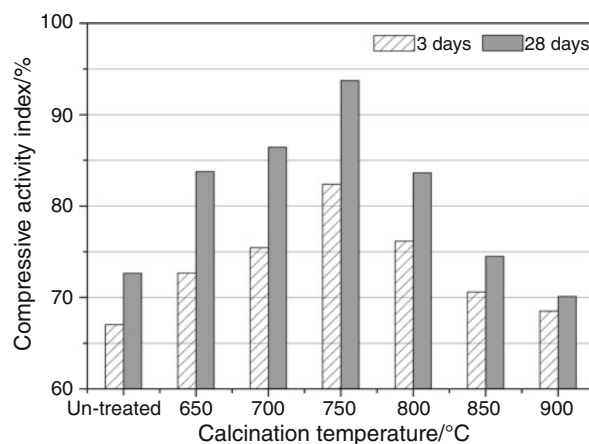


**Table 3** Elemental compositions of points in Fig. 5 determined by X-ray EDS method

Tested point	Elemental composition/%			
	Ca	Si	O	Al
1	3.19	30.7	52.78	13.51
2	6.54	28.3	54.07	12.45
3	17.24	13.55	63.35	8.38
4	22.97	17.83	62.07	9.72
5	15.57	15.32	60.19	9.24

pre-hydrated in water for 3 days before calcination at different temperatures. Both 3 and 28 days compressive activity indexes of fly ash increased significantly after calcination as shown in Fig. 5, among which fly ash sample calcined at 750 °C presents the highest compressive activity indexes.

The effect of curing age on an activity index of the calcined fly ash samples was also considered at the calcination temperature of 750 °C. Figure 6 indicates that the compressive activity indexes of fly ash samples increase as the curing time proceeds. When the curing time exceeds 7 days (corresponding to hydration degree of about 5%), the compressive activity indexes of fly ash samples decrease gradually. It can be inferred that the optimal surface cementitious properties of fly ash can be achieved at a certain curing time or hydration degree. The dehydration and rehydration degree of fly ash can be controlled by the hydration degree of fly ash before calcination, which is usually controlled by the curing time (selected in this experiment), curing temperature, and

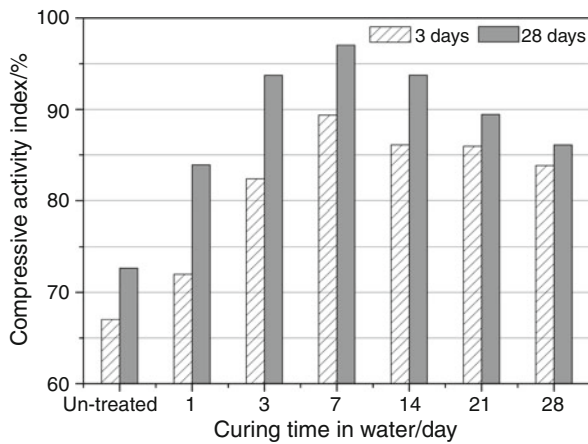


**Fig. 5** Compressive strength activity indexes of fly ash samples calcined at different temperatures (pre-hydrated for 3 days)

curing conditions (lime-saturated water or alkaline lime-saturated water) of fly ash paste.

### Gap-graded BCF

Blended cements with low clinker content were prepared by mixing fine BFS fraction (<8 μm), middle clinker fraction (8–32 μm) and coarse fly ash fraction (>32 μm) homogeneously according to the gap-graded PSD [3]. The mixture proportions of gap-graded blended cements are listed in Table 4. A Portland cement was also prepared by co-grinding, and the Blaine specific surface area of the Portland cement was controlled to be in the range of



**Fig. 6** Compressive strength activity indexes of fly ash samples pre-hydrated for different ages (calcined at 750 °C)

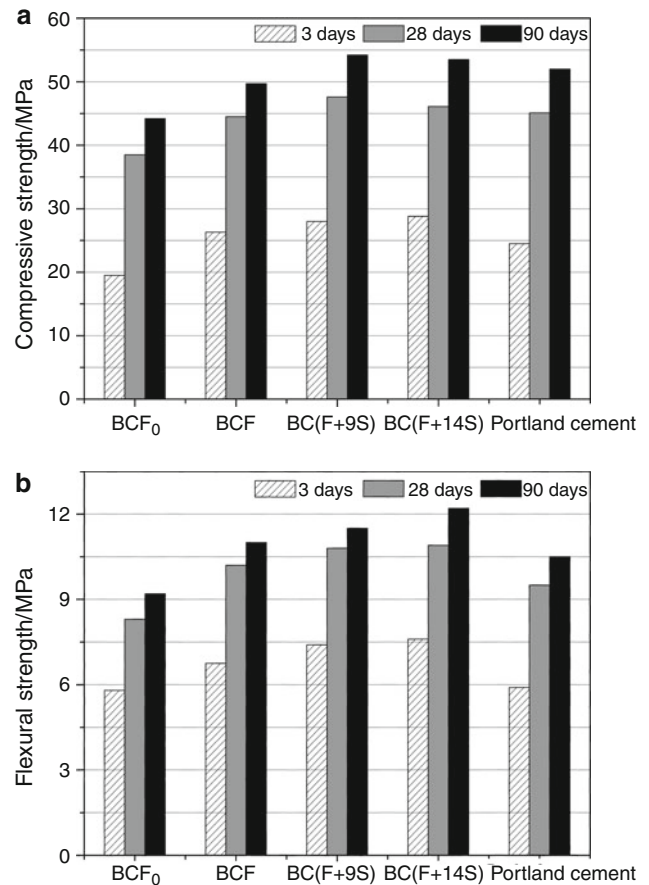
350–360 m<sup>2</sup> kg<sup>-1</sup>, which is seen to be equal to that of the gap-graded blended cements.

Water requirement for normal consistency and setting time of cement pastes

Water requirement for normal consistency and setting time of gap-graded blended cements were determined according to EN 196-3 [18]. Compared to gap-graded blended cement with original fly ash (BCF<sub>0</sub>), the gap-graded BCF have a slightly lower water requirement for normal consistency. More important, both the initial and final setting time are reduced significantly. The observed phenomenon can be attributed to better bonding between the hydration products and calcined fly ash particles because of the rehydration of less crystalline C<sub>2</sub>S.

Compressive and flexural strengths of cement mortars

Compressive and flexural strengths of blended cements were measured according to the method specified in “Dehydration and rehydration processes” section. Figure 7a shows that the 3, 28, and 90 days compressive strengths of gap-graded BCF ash are much higher than those of BCF<sub>0</sub>, and even higher than those of Portland cement. Similar trends are also observed for



**Fig. 7** Compressive and flexural strengths of gap-graded blended cements with BCF<sub>0</sub> or BCF

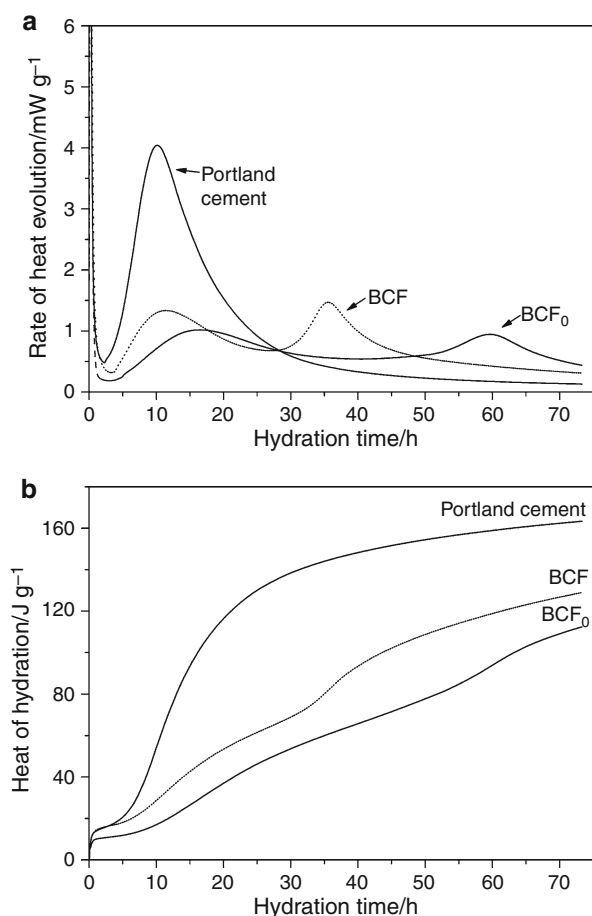
flexural strengths of gap-graded blended cements as shown in Fig. 7b. Fine BFS fraction has higher strength contribution ratio than the corresponding cement clinker fraction [5], and surface cementitious properties of coarse fly ash can be improved by dehydration and rehydration processes. As a result, both early and late mechanical properties of the gap-graded blended cements with only 25% cement clinker and 39% calcined coarse fly ash can be higher than those of 100% Portland cement. The results indicate that the mechanical properties of coarse fly ash incorporated blended cements are

**Table 4** Mixture proportions, water requirement, and setting time of gap-graded blended cements

Fraction/ $\mu\text{m}$	<8	8–32	32–80	Water requirement for normal consistency	Setting time/min	
					Initial	Final
Content/volume/%	36	25	39			
BCF <sub>0</sub>	BFS	Clinker	Fly ash (original)	0.325	183	254
BCF	BFS		Fly ash (calcined)	0.323	142	225
BC(F+9S)	BFS		30% Fly ash (calcined) + 9% steel slag	0.318	140	202
BC(F+14S)	BFS		25% Fly ash (calcined) + 14% steel slag	0.313	148	217
Portland cement	100%	Clinker		0.295	135	197

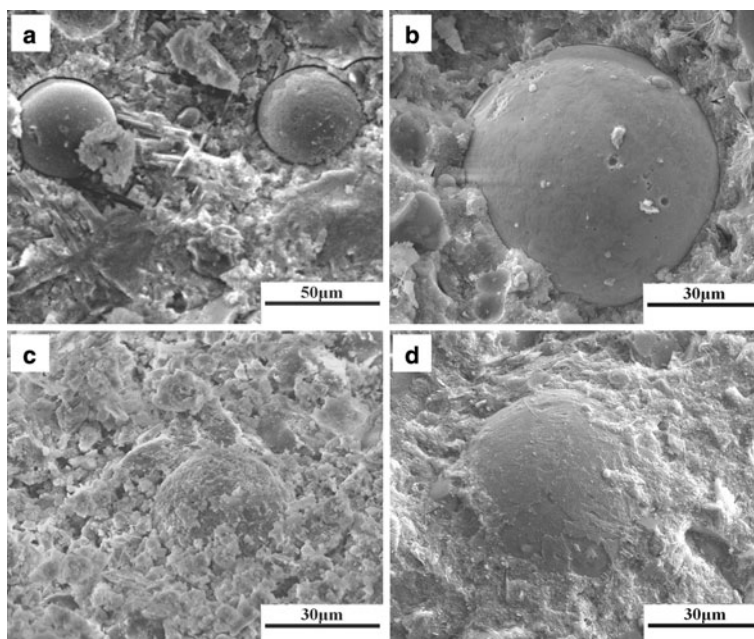
Note: 5% of gypsum dihydrate by mass of cementitious materials was added for all cements in Table 4





**Fig. 8** Heat evolution of gap-graded BCF<sub>0</sub> or BCF. **a** Rate of heat evolution, **b** cumulative heat of hydration

**Fig. 9** SEM images of hardened gap-graded BCF<sub>0</sub> or BCF. **a** BCF<sub>0</sub> cured for 3 days; **b** BCF<sub>0</sub> cured for 28 days; **c** BCF cured for 3 days; **d** BCF cured for 28 days



improved dramatically through surface cementitious modification.

#### Heat evolution of cement pastes

The heat evolution curves of cement pastes made at a water-to-cementitious material mass ratio of 0.5 were tested as the method specified in “Mineral phase changes during calcination” section. Different from heat evolution of Portland cement [19] and normal blended cements [20, 21], the calorimetric curves of gap-graded blended cement pastes show an additional peak (occurring at 30–70 h) due to the hydration of fine BFS particles as shown in Fig. 8a. Clearly, exothermal peaks of BCF appear earlier and show higher value compared with those of BCF<sub>0</sub>. As a result, the cumulative heat of hydration of BCF is slightly higher than that of the BCF<sub>0</sub> during all tested ages (see Fig. 8b). It can be inferred that the hydration of cement clinker and fine BFS is accelerated, because calcined fly ash particles provide larger amount of nucleation sites for hydration products than the original fly ash particles [22].

#### Microstructures of hardened cement pastes

Cement pastes made at water to binder ratio of 0.5 were cast into plastic bags and sealed before placed in a  $20 \pm 1$  °C water bath. Small pieces taken from different parts of the hardened pastes were put into ethyl alcohol to stop hydration after 1, 3, and 28 days curing, then vacuum-oven-dried at 65 °C for at least 48 h. Their microstructures were observed using a scanning electric microscope (SEM, Nano 430, 10 kV). Fly ash particles remain as a clean

surface in BCF<sub>0</sub> after being cured for 3 and 28 days, and there is an obvious gap between fly ash particles and hydration products as shown in Fig. 9a and b. For gap-graded BCF, certain amounts of hydration products is observed on the surface of fly ash particles after 3 days curing (Fig. 9c), implying better bonding between the fly ash particles and hydration products due to rehydration of new generated nesosilicate. As time proceeds, the microstructure of hardened paste becomes denser, and the bonding between the hydration products and fly ash particles is strengthened as shown in Fig. 9c.

## Conclusions

C–S–H gel is mainly transformed into a new nesosilicate, similar to a less crystalline C<sub>2</sub>S, during the calcination at 750 °C. Rehydration of new generated nesosilicate on the surface of coarse fly ash leads to a better bonding between coarse fly ash particles and hydration products. The formation of melilite from hydration products is also noticed at 900 °C, however, this will not contribute to the rehydration properties of calcined fly ash. Gap-graded BCF present a reduced setting time and a slightly higher heat evolution. Bonding between the fly ash particles and hydration products is improved dramatically due to the rehydration of nesosilicate. As a result, both the early and late mechanical properties of gap-graded blended cements contenting 25% cement clinker and 39% calcined fly ash are higher than those of 100% Portland cements. Compared to Portland cement, gap-graded blended cements with about 30% calcined coarse fly ash shows huge economic benefits and much lower energy consumption.

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