Cement & Concrete Composites 34 (2012) 1024–1032

Contents lists available at SciVerse ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Micro-structural development of gap-graded blended cement pastes containing a high amount of supplementary cementitious materials

Tongsheng Zhang, Qijun Yu *, Jiangxiong Wei, Peng Gao, Peixin Chen, Jie Hu

School of Materials Science and Engineering, South China University of Technology, 510640 Guangzhou, People's Republic of China

ARTICLE INFO

Article history:
Received 5 January 2012
Received in revised form 12 June 2012
Accepted 16 June 2012
Available online 23 June 2012

Keywords:
Microstructure
Gap-graded blended cement
Hydration degree
Hydration product
Pore size distribution

ABSTRACT

To clarify the strength improvement mechanism of gap-graded blended cements with a high amount of supplementary cementitious materials, phase composition of hardened gap-graded blended cement pastes was quantified, and compared with those of Portland cement paste and reference blended cement (prepared by co-grinding) paste. The results show that the gap-graded blended cement pastes containing only 25% cement clinker by mass have comparable amount of gel products and porosity with Portland cement paste at all tested ages. For gap-graded blended cement pastes, about 40% of the total gel products can be attributed to the hydration of fine blast furnace slag, and the main un-hydrated component is coarse fly ash, corresponding to un-hydrated cement clinker in Portland cement paste. Further, pore size refinement is much more pronounced in gap-graded blended cement pastes, attributing to high initial packing density of cement paste (grain size refinement) and significant hydration of BFS.

1. Introduction

Utilization of industrial by-products as supplementary cementitious material (SCM) is an effective way not only to cost savings of cement manufacturing, but also to resources and energy savings and environment protection [1,2]. Blended cements usually give a low early strength due to the low hydraulic or pozzolanic activity of SCM, which also limits the substitution level of SCM in blended cement. Bentz proposed that high performance blended cements can be prepared by mixing fine SCM (<10 μm) and coarse cement clinker, these cements also present desirable volume stability and durability [3,4]. Since coarse cement clinker particles (>32 μm) have very low hydration degree even at late ages, the replacement of coarse cement clinker particles by inert filler particles is also suggested, and blended cements prepared by fine cement clinker and coarse inert fillers show only slightly decrease in compressive strengths [5–7]. The above mentioned investigations prove that high performance blended cements with large amount of SCM can be prepared by arranging cementitious materials in proper fractions based on their hydraulic activities.

Zhang proposed a gap-graded particle size distribution (PSD), in which cement particles are divided into three or five fractions, and gap-graded blended cement pastes present a high packing density as voids are filled in, grade by grade [8,9]. Cementitious efficiency of blended cement components can be optimized by arranging SCM with high activity, cement clinker and SCM with low activity (or inert fillers) in fine, middle size and coarse fractions, respectively [10]. High performance gap-graded blended cements with low clinker content can be prepared by arranging cementitious materials in the gap-graded PSD according to their hydraulic activities. For instance, both 3 days and 28 days compressive strengths of the gap-graded blended cements with only 25% cement clinker by mass can be comparable with or higher than those of Portland cement [9,10]. However, the strength improvement mechanism of gap-graded blended cement has not been clearly explained.

The objective of the present study is to clarify the strength improvement mechanism of gap-graded blended cements. The micro-structural development of gap-graded blended cement pastes, Portland cement paste and reference blended cement (prepared by co-grinding) paste were investigated. Based on the quantitative analysis of gel products, un-hydrated components and porosity of hardened cement pastes, the strength improvement mechanism was discussed in detail. The results will contribute to reducing CO_2 emissions and obtaining substantial energy and cost savings, by substituting larger amount of cement clinker with SCM.

2. Preparation of gap-graded blended cements

Portland cement clinker, blast furnace slag (BFS), and low calcium fly ash (a Class F fly ash according to ASTM C 618 [11]) were ground and then classified by an air classifier. By changing operational parameters, size fractions of cementitious materials required by the gap-graded PSD were obtained. The PSDs of cementitious material fractions used in the experiment are given in Fig. 1. The

* Corresponding author. Tel./fax: +86 020 87114233.
E-mail address: concyuq@scut.edu.cn (Q. Yu).

0958-9465/$ - see front matter
http://dx.doi.org/10.1016/j.cemconcomp.2012.06.010

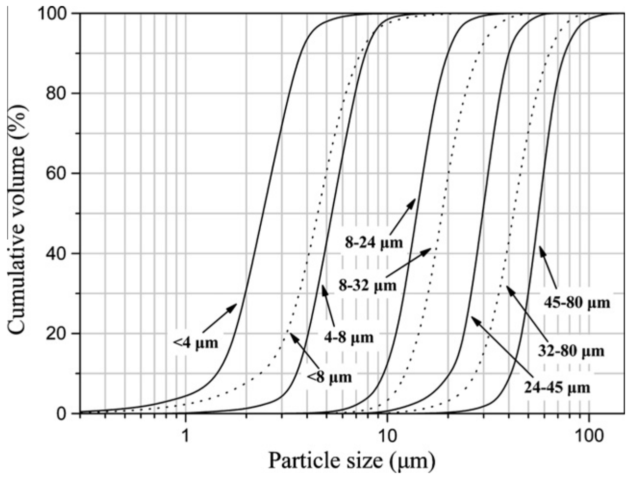

Fig. 1. Particle size distributions of cementitious material fractions used in the experiment.

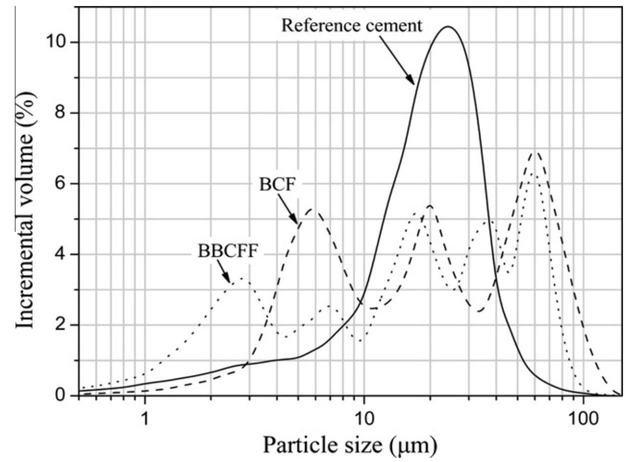

Fig. 2. Particle size distributions of gap-graded blended cements and reference cement.

chemical compositions of raw materials and classified cementitious material fractions are given in Table 1, from which nearly no deviation in chemical composition is observed for given cementitious material.

The mixture proportions of gap-graded blended cements and reference cement are the same as shown in Table 2, while the fineness of each component is quite different. The gap-graded blended cements (BCF stands for gap-graded blended cement prepared by fine BFS fraction (<8 μm), middle size cement clinker fraction (8–32 μm) and coarse fly ash fraction (32–80 μm), and BBCFF stands for gap-graded blended cement prepared by fine BFS fractions (<4 μm and 4–8 μm), middle size cement clinker fraction (8–24 μm) and coarse fly ash fractions (24–45 μm and 45–80 μm)) were prepared by mixing each cementitious material fraction to obtain as much as possible of homogeneity, while the reference cement and a Portland cement were prepared by co-grinding, and the Blaine specific surface areas of these two cements were controlled to be in the range of 350–360 m^2/kg, which is seen to be equal to those of the gap-graded blended cements approximately. Fig. 2 shows that the incremental PSD of reference cement has only one peak, and those of BCF and BBCFF cements present three and five peaks, respectively. It can be inferred that cements prepared by co-grinding have a narrow PSD, while the gap-graded blended cements present a wide PSD, resulting in a high initial packing density of cement paste.

Table 1
Chemical compositions of raw materials and classified raw material fractions used the experiment.

Material	Density (g/cm^3)	Chemical composition (%)									
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI	
Quartz sand		2.65	99.16	0.36	0.12	0.18	0.06	0.02	0.01	0.02	0.02
Portland cement clinker	Original	3.14	21.6	4.35	2.95	63.81	1.76	0.51	0.16	1.06	1.19
	8–24 μm	3.15	21.26	4.35	2.75	63.61	1.80	0.58	0.21	1.21	1.59
	8–32 μm	3.15	21.34	4.42	2.76	63.74	1.75	0.49	0.18	1.20	1.35
BFS	Original	2.90	35.22	12.15	0.25	37.08	11.25	0.49	0.25	1.19	−0.36
	<4 μm	2.88	34.98	12.00	0.24	36.54	11.42	0.51	0.25	1.48	1.37
	4–8 μm	2.89	35.72	12.26	0.26	36.56	11.28	0.48	0.25	1.21	−0.77
	<8 μm	2.89	35.02	12.11	0.34	36.95	11.13	0.49	0.25	1.14	−0.9
Low calcium fly ash	Original	2.56	45.43	24.36	6.70	7.53	1.51	1.23	0.36	1.03	7.88
	24–45 μm	2.56	46.50	24.46	6.68	7.35	1.55	1.08	0.32	0.93	6.72
	45–80 μm	2.56	46.74	25.31	6.74	6.96	1.56	0.97	0.31	0.87	6.57
	32–80 μm	2.57	46.62	25.09	6.63	7.34	1.52	1.05	0.33	0.91	6.50

Note: LOI, loss on ignition.

Table 2
Mixture proportions of gap-graded blended cements, Portland cement and reference cement.

BBCFF	Fraction (μm)	<4	4–8	8–24	24–45	45–80
	Content	25%	11%	25%	19%	20%
	Cementitious material	BFS	BFS	Cement clinker	Fly ash	Fly ash
BCF	Fraction (μm)	<8		8–32	32–80	
	Content	36%		25%	39%	
	Cementitious material	BFS		Cement clinker	Fly ash	
Portland cement	100% Cement clinker					
Reference cement	36% BFS + 25% Cement clinker + 39% fly ash					

Note: 5% of gypsum dihydrate by mass of cementitious material was added for all the cements in this table.

3. Experiment and results

3.1. Fundamental properties of blended cements

Water requirement for normal consistency of blended cements was determined according to EN 196-3 [12]. The maximum volume concentration of solids was used to characterize the packing density of cement paste, and the method is specified in the literature [13]. The compressive strengths of cement mortars were tested according to EN 196-1 [14].

Due to the fact that the fly ash used contains a high content of un-burnt carbon and a large amount of porous particles, blended cement pastes show higher water requirement for normal consistency than Portland cement paste as shown in Table 3. Gap-graded blended cement pastes present much higher maximum volume concentration of solids than the reference cement paste and Portland cement paste, especially for BBCFF cement paste. Both 3 days and 28 days compressive strengths of the gap-graded blended cements are much higher than those of reference cement. It should be noted that the compressive strengths of BBCFF cement can be comparable with those of Portland cement.

3.2. Quantitative analysis of phase composition of hardened cement paste

Although water requirement for normal consistency of blended cements varies so significantly due to different fine particle content, cement pastes or mortars with equal fluidity are largely used in practical application. Therefore, in this study cement pastes with normal consistency were cast into plastic bags and sealed before placing the pastes in a 20 ± 1 °C water bath. Small pieces taken from different parts of the hardened paste were put into ethyl alcohol to terminate their hydration after curing for 1, 3, 7, 14 and 28 days, then vacuum-oven-dried at 65 °C for at least 48 h [9].

3.2.1. The amount of un-hydrated cement clinker in blended cement pastes

The amount of un-hydrated cement clinker was determined by quantitative X-ray diffraction (QXRD) under the conditions of 40 kV, 15 mA, Cu $K\alpha_1$, 0.05° 2θ step size, and 3s/step using K-value method, in which α-Al_2O_3 was used as internal standard substance [15]. Mixtures of α-Al_2O_3 (15% by mass) and blended cement with different cement clinker content as shown in Table 4 were ground and subjected to QXRD measurement. The diffraction peak at d = 0.276 nm (an overlap diffraction peak of C_3S and C_2S) was used for quantitative analysis as shown in Fig. 3. Fig. 4 indicates that the intensity of the diffraction peak (d = 0.276 nm) increases linearly with the increase of cement clinker content.

The dried samples were also ground and mixed with 15% (by mass) α-Al_2O_3, then QXRD was performed on the mixtures. According to the relationship between the intensity of the diffraction peak (d = 0.276 nm) and the cement clinker content in Fig. 4, the content of un-hydrated cement clinker remained in the hardened cement pastes can be obtained, then the hydration degree of cement clinker can be calculated. The results are presented in Fig. 5. The hydration degree of cement clinker in the reference cement paste

Table 4
Mixture proportions of α-Al_2O_3, cement clinker, BFS and fly ash for QXRD measurement.

Sample	Mixture proportion (%)		
	α-Al_2O_3	Cement clinker	(BFS + fly ash)[a]
1	15	0	85
2	15	5	80
3	15	10	75
4	15	15	70
5	15	20	65
6	15	25	60
7	15	30	55

[a] The mass ratio of BFS to fly ash in the mixtures equals to that in gap-graded blended cements (36:39).

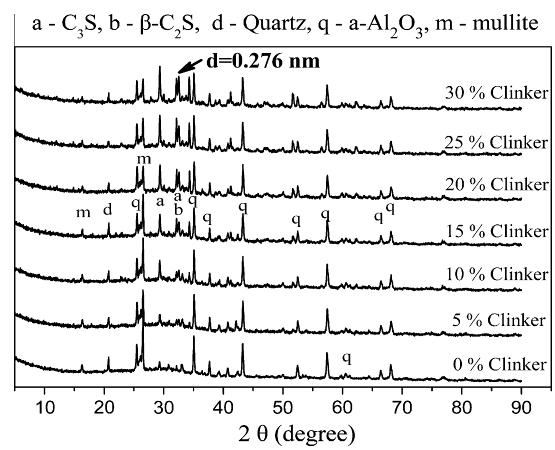

Fig. 3. X-ray diffraction patterns of the mixtures of α-Al_2O_3 and blended cement with different cement clinker content.

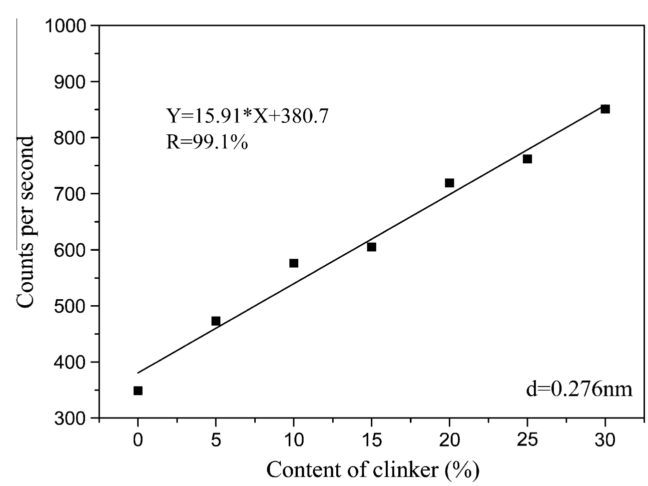

Fig. 4. Relationship between the intensity of diffraction peak at d = 0.276 nm and cement clinker content in blended cements.

Table 3
Water requirement for normal consistency, maximum volume concentration of solids and mortar strengths of gap-graded blended cements.

Cement	Reference cement	Portland cement	BCF	BBCFF
Water requirement for normal consistency	0.346	0.295	0.325	0.334
Maximum volume concentration of solids (%)	45.40	49.12	50.17	53.48
Compressive strength (MPa)				
3 days	11.3 ± 0.1	23.5 ± 0.2	19.3 ± 0.2	24.1 ± 0.2
28 days	29.6 ± 0.3	45.0 ± 0.4	41.8 ± 0.3	43.8 ± 0.3

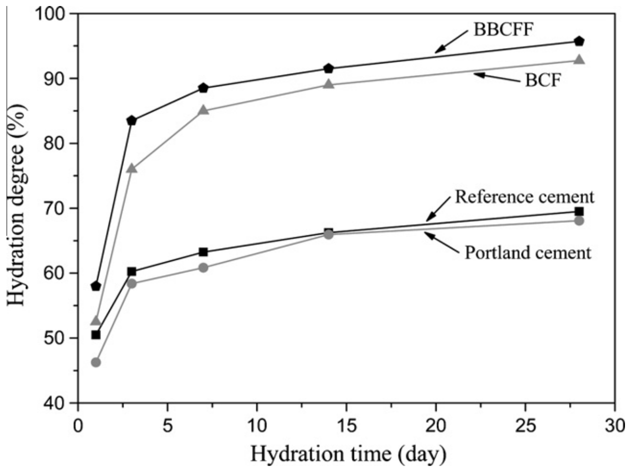

Fig. 5. The hydration degree of cement clinker in Portland cement, reference cement, BBCFF and BCF cement pastes.

is slightly higher than that in Portland cement paste in the first 7 days, while no obvious difference in hydration degree of cement clinker was observed after 14 days. For the gap-graded blended cements, the hydration degree of cement clinker increases significantly in the first 3 days, and can be higher than 90% after 28 days curing.

3.2.2. The $Ca(OH)_2$ content in blended cement pastes

Differential thermal analysis–thermogravimetry (DTA–TG) measurement (heating rate of 10 °C/min in nitrogen atmosphere) was used to determine the $Ca(OH)_2$ content in cement paste [16]. The DTA curves in Fig. 6 show a sharp endothermal peak between 400 and 500 °C due to the decomposition of $Ca(OH)_2$ [17], therefore the $Ca(OH)_2$ content can be calculated by estimating the corresponding weight loss from TG curves. A minor endothermal peak around 700 °C (attribute to the decomposition of $CaCO_3$) is also observed due to the unavoidable carbonation of $Ca(OH)_2$ during the curing and drying processes [18]. In the present study, the $Ca(OH)_2$ content in the cement paste is considered as the sum of $Ca(OH)_2$ that remained in cement paste and $Ca(OH)_2$ carbonated into $CaCO_3$.

To clarify the decomposition temperature ranges of $Ca(OH)_2$ and $CaCO_3$, differential thermogravimetric (DTG) curves of BCF cement pastes were plotted as shown in Fig. 7. It is more reasonable that 40–400 °C, 400–500 °C, and 650–730 °C are regarded as the decomposition temperature ranges of gel products (mainly C–S(A)–H and AF_t), $Ca(OH)_2$, and $CaCO_3$, respectively [19,20]. The $Ca(OH)_2$ content in the blended cement pastes determined from TG curves was shown in Fig. 8. Due to a high amount of un-hydrated cement clinker, the $Ca(OH)_2$ content in the reference cement paste is relatively lower than those in gap-graded blended cement pastes. Further, the $Ca(OH)_2$ content in BBCFF cement paste decreases significantly after 3 days due to the hydration of fine (<4 μm) BFS particles, while only a slightly decrease of $Ca(OH)_2$ content is observed after 7 days for BCF cement paste.

3.2.3. Hydration degree of BFS in blended cement paste

Since the coarse low calcium fly ash fractions used has a low pozzolanic activity, fly ash in blended cement (both gap-graded blended cements and reference cement) pastes is regarded as inert material. Therefore, the hydration degree of BFS can be determined by estimating the $Ca(OH)_2$ content consumed by its hydration as specified in the literatures [19,21]. The $Ca(OH)_2$ content (determined by TG) in Portland cement pastes with different hydration degree are shown in Fig. 9, from which it can be deduced that 1 g completely hydrated Portland cement generates 0.354 g

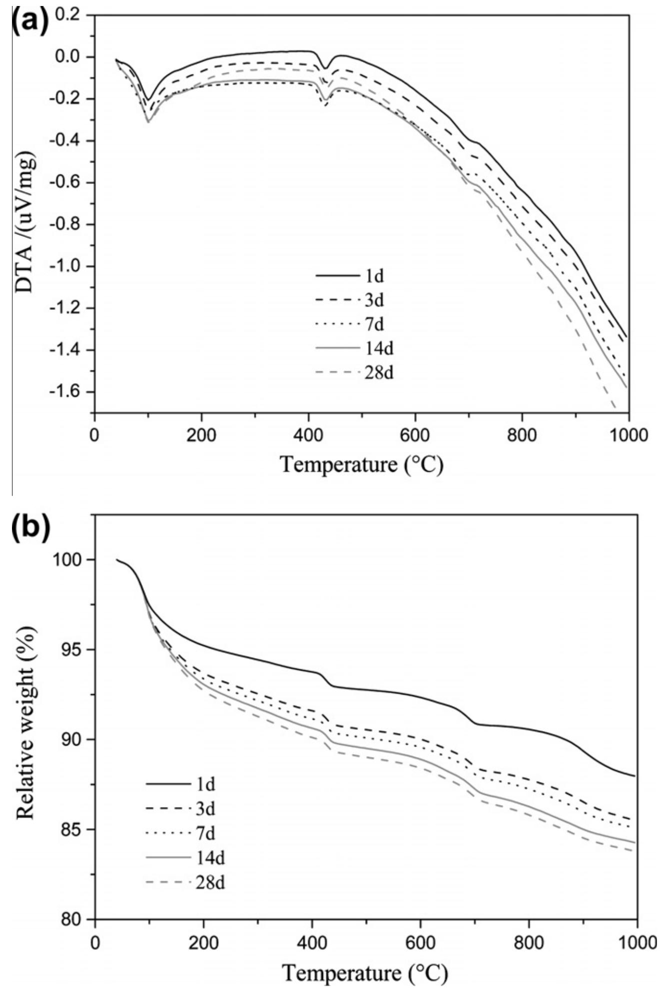

Fig. 6. DTA-TG curves of BCF cement pastes cured for different ages. (a) DTA curves. (b) TG curves.

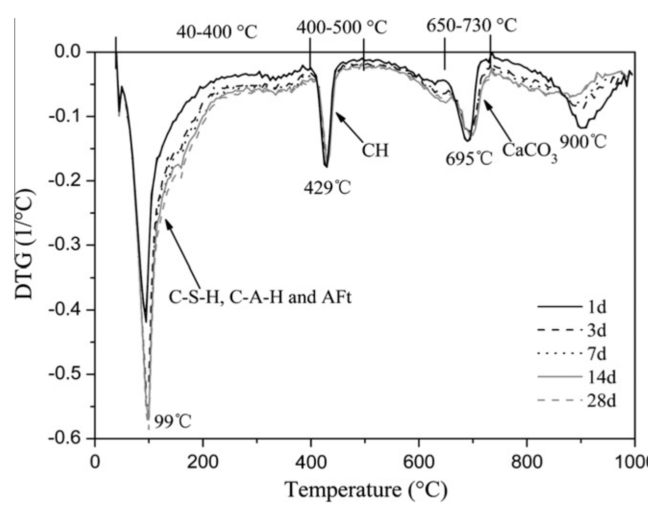

Fig. 7. Differential TG curves of BCF cement pastes cured for different ages.

$Ca(OH)_2$. Based on the hydration degree of cement clinker in blended cement paste (Section 3.2.1, Fig. 5), the $Ca(OH)_2$ content generated from the hydration of cement clinker was calculated as shown in Fig. 10. The $Ca(OH)_2$ content consumed by BFS hydration can be obtained by Eq. (1) and is shown in Fig. 11:

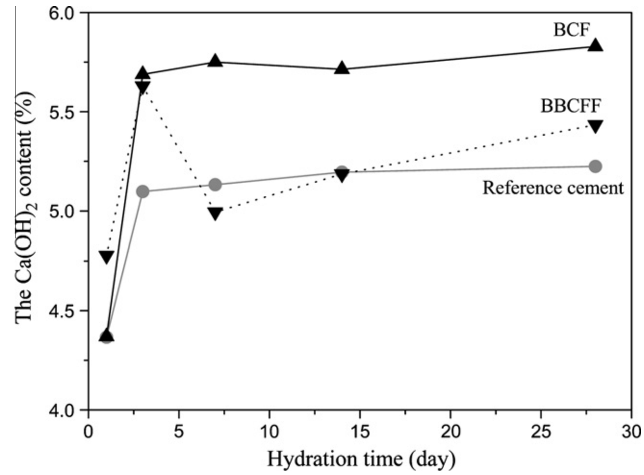

Fig. 8. The $Ca(OH)_2$ content remained in Portland cement, reference cement, BBCFF and BCF cement pastes.

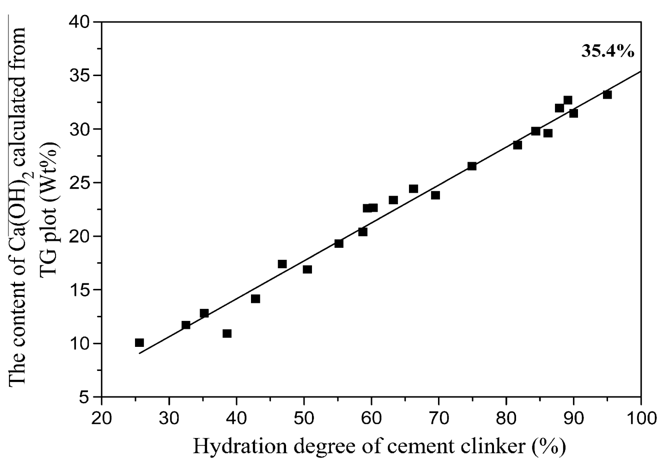

Fig. 9. Relationship between the hydration degree of cement clinker and the amount of $Ca(OH)_2$ generated.

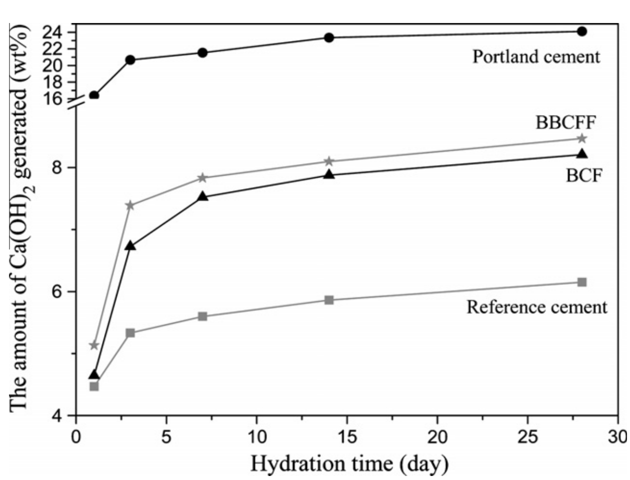

Fig. 10. The amount of $Ca(OH)_2$ generated in Portland cement, reference cement, BBCFF and BCF cement pastes.

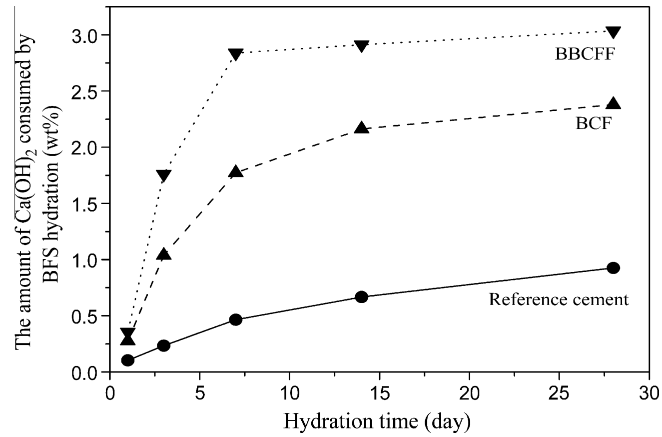

Fig. 11. The amount of $Ca(OH)_2$ consumed by BFS hydration in reference cement, BBCFF and BCF cement pastes.

$$CH_{consumed} = CH_{generated} - CH_{remained} \tag{1}$$

where $CH_{consumed}$, $CH_{generated}$, and $CH_{remained}$ refer to the amount of $Ca(OH)_2$ consumed by BFS hydration, generated from cement clinker hydration, and remained in cement paste (determined in Section 3.2.2), respectively.

Meanwhile, the $Ca(OH)_2$ content consumed by BFS hydration in BFS-$Ca(OH)_2$ paste was also measured, and the hydration degree of BFS was also determined by ethylene diamine tetraacetic acid disodium salt (EDTA) preferential solving method [22]. Fig. 12 shows that the amount of $Ca(OH)_2$ consumed by BFS hydration increases linearly with the increase of the hydration degree of BFS, and it can be inferred that 1 g completely hydrated BFS consumes 0.0915 g $Ca(OH)_2$. The hydration degree of BFS in blended cement paste can be calculated by :

$$\alpha_{BFS} = \frac{CH_{consumed}}{CH_0} \tag{2}$$

where α_{BFS} is the hydration degree of BFS; CH_0 is the amount of $Ca(OH)_2$ consumed by per completely hydrated BFS (9.15% by mass).

The hydration degree of BFS in blended cement pastes calculated by Eq. (2) is given in Fig. 13. Gap-graded blended cement pastes present significantly higher hydration degree of BFS than the reference cement paste at all tested ages, especially for BBCFF cement paste. For instance, the 3 days and 28 days hydration de-

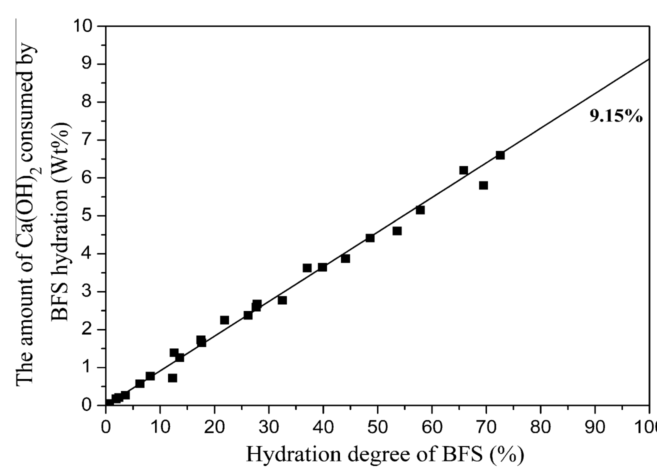

Fig. 12. Relationship between the hydration degree of BFS and the amount of $Ca(OH)_2$ consumed.

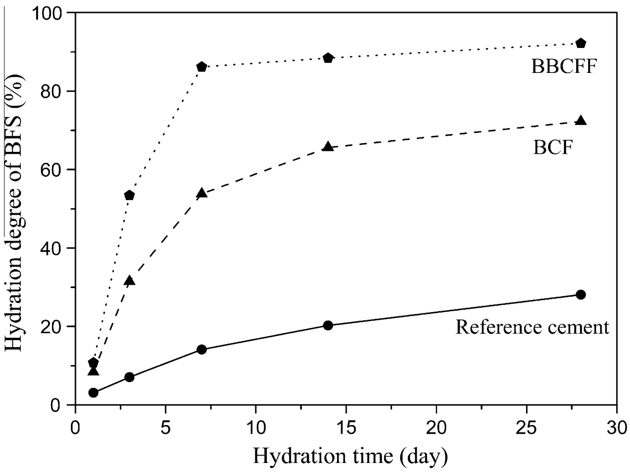

Fig. 13. Hydration degree of BFS in reference cement, BBCFF and BCF cement pastes.

grees of BFS in reference cement paste are 7.1% and 28.1%, respectively. In contrast, the 3 days and 28 days hydration degrees of BFS in BCF cement paste are 31.5% and 72.3% respectively, and can be as high as 53.4% and 92.1% for BBCFF cement paste.

3.2.4. The amount of gel products in blended cement paste

The weight loss of samples in the range of 40–400 °C was used to semi-quantitatively determine the amount of gel products in blended cement pastes. Although the precision of this method is limited, normally it is regarded that a larger weight loss in the range of 40–400 °C means a higher amount of gel products in the cement paste. It can be concluded from Fig. 14 that Portland cement paste has the highest amount of gel products, while reference cement paste presents the lowest amount of gel products at all tested ages. In contrast, gap-graded blended cement pastes have much higher amount of gel products than the reference cement paste, and the amount of gel products in BBCFF cement paste can be comparable with that of Portland cement paste.

3.2.5. Porosity and pore size distribution of hardened cement paste

The porosity and pore size distribution of dried samples were measured by mercury intrusion porosimetry (MIP, Poremaster-60, contact angle: 140.7°) with an operating pressure up to about 500 MPa. Table 5 shows that the reference cement paste has the highest total porosity at all tested ages, while gap-graded blended cement pastes present a much lower porosity. It should be noted that the total porosity of BBCFF cement paste is even lower than that of Portland cement paste after being cured for 28 days. Fig. 15 indicates that a large proportion of pores in the reference cement paste exists in the form of large-size pores (>100 nm) due to small amount of hydration products, which is harmful to the mechanical properties of hardened paste. In comparison with the reference cement paste, the amount of large-size pores in gap-graded blended cement pastes is reduced significantly, and the proportion of fine pores (<50 nm) in gap-graded blended cement pastes is even larger than that of Portland cement paste, especially for BBCFF cement paste. The refinement of pores in gap-graded blended cement pastes can be attributed to high initial packing density of cement paste (grain size refinement) and significant hydration of BFS.

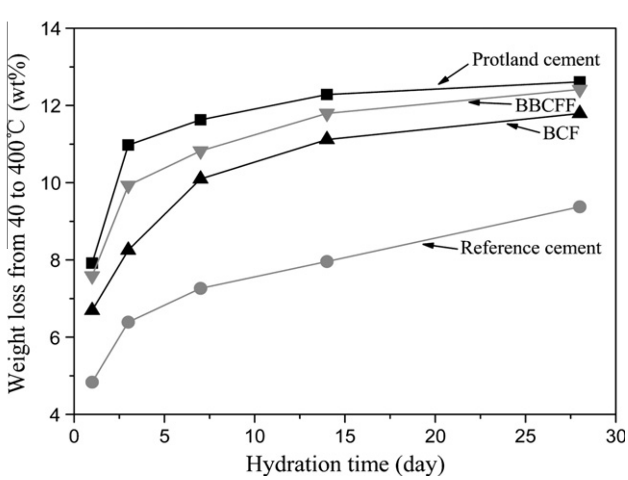

Fig. 14. Weight loss from 40 to 400 °C of Portland cement, reference cement, BBCFF and BCF cement pastes.

Table 5
Porosity of Portland cement, reference cement, BBCFF and BCF cement pastes cured for different ages (vol%).

Curing age (day)	1	3	7	28
Reference cement	42.71	36.3	30.44	25.55
Portland cement	34.47	27.38	22.57	20.03
BCF	36.9	27.43	24.19	21.05
BBCFF	33.29	25.98	21.98	18.95

4. Discussion

4.1. Classification of gel products

In the above analysis, coarse fly ash fractions used is regarded as inert material. To verify if the hypothesis is reasonable, the amount of gel products generated from the hydration of cement clinker, fine BFS and pozzolanic reaction of coarse fly ash were characterized. Gap-graded blended mixtures with the proportions shown in Table 6 were prepared through substituting fine BFS or coarse fly ash fractions by corresponding quartz sand fractions. Specimens were obtained by mixing these mixtures and water at a water/all cementitious materials ratio of 0.334 (water requirement for normal consistency of BBCFF cement). When fine quartz sand powder is used, the specimen is not cement paste anymore. The specimens were cast into plastic bags and sealed before placing the pastes in a 20 ± 1 °C water bath. After curing for 1, 3, 7, 14 and 28 days, the specimens were vacuum-oven-dried and subjected to DTA-TG measurement. The weight loss from 40–400 °C of these specimens is given in Fig. 16. By comparing the difference in weight loss from 40–400 °C of BBCQQ and BBCFF specimens, it can be inferred that the coarse fly ash fractions don't have significant influence on the amount of gel products, indicating that the coarse fly ash fractions in gap-graded blended cement paste can be considered as inert material. Therefore the gel products in BBCFF specimen can be attributed to the hydration of cement clinker and fine BFS, while those in QQCFF specimen is only attributed to the hydration of cement clinker. It can be calculated that gel products generated from the hydration of fine BFS in BBCFF cement paste accounts for 42.2% and 44.0% of the total gel products at 3 days and 28 days, respectively.

4.2. Phase composition of hardened cement paste

Since the porosity and the weight percentages of $Ca(OH)_2$, unhydrated cement clinker, BFS, and fly ash (regarded as inert material) in hardened cement paste were obtained, the volumetric phase composition of hardened cement paste can be calculated as follows. The volume of pores equals to the porosity of hardened

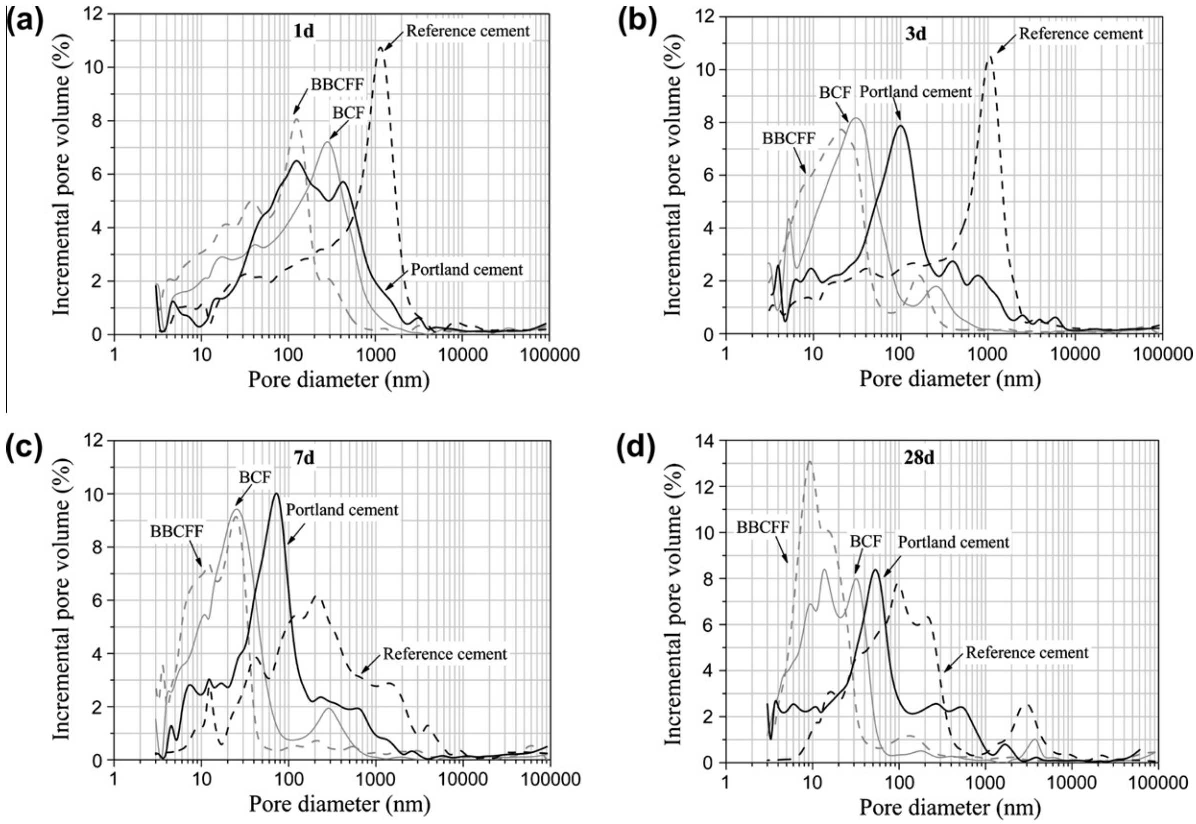

Fig. 15. Pore size distributions of hardened Portland cement, reference cement, BBCFF and BCF cement pastes. (a) Cement pastes cured for 1 day. (b) Cement pastes cured for 3 days. (c) Cement pastes cured for 7 days. (d) Cement pastes cured for 28 days.

Table 6
Mixture proportions of gap-graded blended cements with quartz sand.

Fraction (μm) Content (%)	<4 25	4–8 11	8–24 25	24–45 19	45–80 20
BBCFF	BFS	BFS	**C**	Fly ash	Fly ash
BBCQQ	BFS	BFS	**C**	Quartz sand	Quartz sand
QQCFF	Quartz sand	Quartz sand	**C**	Fly ash	Fly ash
QQCQQ	Quartz sand	Quartz sand	**C**	Quartz sand	Quartz sand

Note: 5% of gypsum dihydrate by mass of cementitious material was added for all the cements in this table.

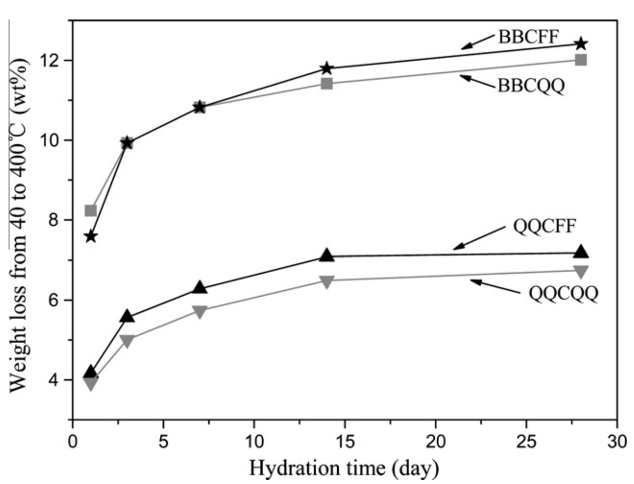

Fig. 16. Weight loss from 40 to 400 °C of gap-graded blended cements with ground quartz sand.

cement paste, therefore the volume of solid phases can be calculated by :

$$V_S = 1 - V_P \quad (3)$$

where V_S and V_P represent volume percentages of solid phase and pores, respectively.

The specific densities of cement clinker, BFS, fly ash can be obtained from Table 1, and that of $Ca(OH)_2$ used is 2.24 g/cm^3 [23]. Therefore, the volume percentages of $Ca(OH)_2$, un-hydrated cement clinker, BFS, and fly ash can be calculated from their weight percentages, thus the volume percentage of gel products can be obtained by :

$$V_G = V_S - V_C - V_B - V_F - V_{CH} \quad (4)$$

where V_G, V_C, V_B, V_F, and V_{CH} are volume percentages of gel products, un-hydrated cement clinker, BFS, fly ash and $Ca(OH)_2$, respectively.

Pores usually are harmful to the strength development of hardened cement paste, while gel products (including AF_t, C–S–H and C–A–H gels) are the source of strength development. Further, the binding between "micro-aggregates" ($Ca(OH)_2$ and un-hydrated

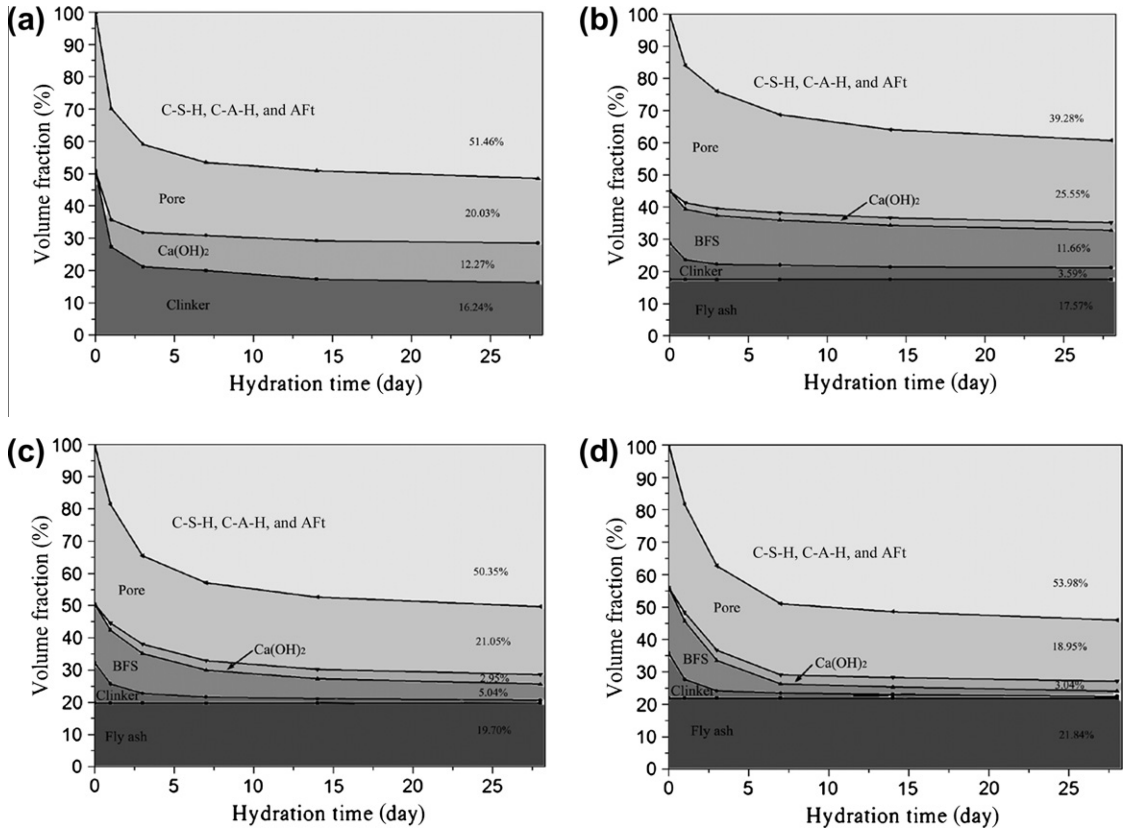

Fig. 17. Phase composition of hardened Portland cement, reference cement, BBCFF and BCF cement pastes. (a) Portland cement paste. (b) Reference cement paste. (c) BCF cement paste. (d) BBCFF cement paste.

Table 7
Phase composition of hardened Portland cement, reference cement, BBCFF and BCF cement pastes cured for 28 days (volume percentage).

Category	Gel products	Pore		"Micro-aggregates"			
Phase	C–S–H, C–A–H gel and AFt	Porosity	Cement clinker	$Ca(OH)_2$	BFS	Fly ash	Sum.
Portland cement	51.46	20.03	16.24	12.27	0	0	28.51
Reference cement	39.28	25.55	3.59	2.35	11.66	17.57	35.17
BCF	50.35	21.05	0.92	2.94	5.04	19.70	28.60
BBCFF	53.98	18.95	0.60	3.04	1.58	21.84	27.06

components) and gel products also has significant influence on the strength of hardened cement paste. Thus, phases in hardened cement paste can be classified into three categories, as gel products, pore, and "micro-aggregates".

Fig. 17 and Table 7 show that the volume percentage of gel products in Portland cement paste cured for 28 days is 51.5%, while the volume percentages in BCF and BBCFF cement pastes are 50.4% and 54.0% respectively, decreasing to 39.3% for the reference cement paste. For gap-graded blended cement pastes and Portland cement paste, no obvious difference in porosity is observed at all tested ages. However, the porosity of reference cement paste is much higher than those of gap-graded blended cement pastes. Portland cement paste cured for 28 days contains 16.2% un-hydrated cement clinker and 12.3% $Ca(OH)_2$. In contrast, the amounts of un-hydrated cement clinker and $Ca(OH)_2$ in blended cement paste are reduced sharply. Compared to the reference cement paste, gap-graded blended cement pastes have lower contents of un-hydrated cement clinker and BFS. The volume percentage of the so-called "micro-aggregates" in gap-graded blended cement pastes is about 28%, which nearly equals to that in Portland cement paste, while the volume percentage of "micro-aggregates" in the reference cement paste can be as high as 35.2%.

By arranging BFS and cement clinker in fine and middle fractions respectively, both cement clinker and BFS in gap-graded blended cement pastes present much higher hydration degree than those in reference cement paste. As a result, the volume percentage of gel products in gap-graded blended cement pastes can be comparable with that of Portland cement paste, although only 25% cement clinker by mass is used. The main un-hydrated component in gap-graded blended cement pastes is coarse fly ash, corresponding to un-hydrated cement clinker in Portland cement paste. Due to "grain size refinement" and significant hydration of BFS, the microstructure of gap-graded blended cement pastes appears even denser than that of Portland cement paste, especially for BBCFF cement paste. Therefore the compressive strengths of gap-graded blended cements are significantly higher than those of the reference cement, and only slightly lower than those of Portland cement due to the poor binding between coarse fly ash and gel products [24].

5. Conclusions

Gap-graded blended cement pastes containing 25% cement clinker have a comparable amount of gel products and porosity with Portland cement paste at all tested ages, and about 40% of the total gel products is attributed to the hydration of fine BFS in gap-graded blended cement paste. Pore size refinement is much more pronounced in gap-graded blended cement pastes than in Portland cement paste, due to a high initial packing density of cement paste (grain size refinement) and significant hydration of BFS. The "micro-aggregates" in gap-graded blended cement pastes mainly consists of coarse fly ash, corresponding to the un-hydrated cement clinker and $Ca(OH)_2$ in Portland cement paste, otherwise the volume percentage of "micro-aggregates" in gap-graded blended cement pastes nearly equals to that in Portland cement paste. Gap-graded blended cement pastes present a similar micro-structural development to Portland cement paste, resulting in significant improvement of mechanical properties of hardened cement paste. The results give a better understanding of the micro-structural development of gap-graded blended cement paste.

Acknowledgments

This work was funded by 973 National Foundational Research of China (No. 2009CB623104), National Natural Science Foundation of China (No. 51072058), and the Joint Foundation of the National Natural Science Foundation of China (No. U1134008), their financial supports are gratefully acknowledged.

References

[1] Kumar S, Kumar R, Bandopadhyay A. Innovative methodologies for the utilization of wastes from metallurgical and allied industries. Resour Conserv Recy 2006;48(3):301–14.
[2] Rafat S. Waste materials and by-products in concrete. Berlin: Springer; 2008.
[3] Bentz DP, Haecker CJ. An argument for using coarse cements in high-performance concretes. Cem Concr Res 1999;29(4):615–8.
[4] Bentz DP, Hansen AS, Guynn JM. Optimization of cement and fly ash particle sizes to produce sustainable concretes. Cem Concr Compos 2011;33(6):824–31.
[5] Bentz DP, Conway JT. Computer modeling of the replacement of "coarse" cement particles by inert fillers in low w/c ratio concretes: hydration and strength. Cem Concr Res 2001;31(3):503–6.
[6] Bentz DP. Modeling the influence of limestone filler on cement hydration using CEMHYD3D. Cem Concr Compos 2006;28(2):124–9.
[7] Bentz DP. Replacement of coarse cement particles by inert fillers in low w/c ratio concretes II. Exp validation. Cem Concr Res 2005;35(1):185–8.
[8] Zhang TS, Yu QJ, Wei JX, Zhang PP, Chen PX. A gap-graded particle size distribution for blended cements: analytical approach and experimental validation. Powder Technol 2011;214(2):259–68.
[9] Zhang TS, Yu QJ, Wei JX, Zhang PP. A new gap-graded particle size distribution and resulting consequences on properties of blended cement. Cem Concr Compos 2011;33(5):543–50.
[10] Zhang TS, Yu QJ, Wei JX, Zhang PP. Efficient utilization of cementitious materials to produce sustainable blended cement. Cem Concr Compos 2012;34(5):692–9.
[11] ASTM C 618-03. Standard specification for coal fly ash and raw or calcined natural pozzolan for use as a mineral admixture in Portland cement concrete. New York: American Society for Testing and Materials; 2003.
[12] EN 196-3. Methods of testing cement: determination of water requirement for normal consistency. London: British Standards Institution; 2005.
[13] Kwan AKH, Fung WWS. Packing density measurement and modeling of fine aggregate and mortar. Cem Concr Compos 2009;31(6):349–57.
[14] EN 196–1. Methods of testing cement: determination of strength. London: British Standards Institution; 2005.
[15] Jansen D, Goetz-Neunhoeffer F, Lothenbach B, Neubauer J. The early hydration of ordinary Portland cement (OPC): an approach comparing measured heat flow with calculated heat flow from QXRD. Cem Concr Res 2012;42(1):134–8.
[16] Moukwa M, Farrington S, Youn D. Determination of $Ca(OH)_2$ in hydrated cement paste by differential scanning calorimetry. Thermochim Acta 1992;195(1):231–7.
[17] Vedalakshmi R, Raj AS, Srinivasan S, Babu KG. Quantification of hydrated cement products of blended cements in low and medium strength concrete using TG and DTA technique. Thermochim Acta 2003;407(1):49–60.
[18] Badanoiu A, Georgescu M, Puri A. The study of 'DSP' binding systems by thermogravimetry and differential thermal analysis. J Therm Anal Cal 2003;74(1):65–75.
[19] Vedalakshmi R, Raj SA, Srinivasan S, Babu GK. Quantification of hydrated cement products of blended cements in low and medium strength concrete using TG and DTA technique. Thermochim Acta 2003;407(1–2):49–60.
[20] Ubbriaco P, Calabrese D. Solidification and stabilization of cement paste containing fly ash from municipal waste. Thermochim Acta 1998;321(1–2):143–50.
[21] Sha W, Pereira GB. Differential scanning calorimetry study of normal Portland cement paste with 30% fly ash replacement and of the separate fly ash and ground granulated blast furnace slag powders. In: Proceedings of the Seventh CANMET/ACI international conference on fly ash, silica fume, slag and natural pozzolans in concrete, Detroit: ACI; 2001.
[22] Zhang TS, Yu QJ, Wei JX, Zhang PP, Li S. Effect of size fraction of ground granulated blast furnace slag on its strength contribution and hydraulic activity. Adv Sci Lett 2011;4(3):1286–91.
[23] Taylor HFW. Cement chemistry. 2nd ed. London: Thomas Telford; 1997.
[24] Zhang TS, Yu QJ, Wei JX, Zhang PP, Chen PX. Improvement of surface cementitious properties of coarse fly ash by dehydration and rehydration processes. J Therm Anal Calorim 2011. http://dx.doi.org/10.1007/s10973-011-1697-0.