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Efficient utilization of cementitious materials to produce sustainable blended cement

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ABSTRACT

To achieve sustainable development of cement industry, cementitious efficiency of different cement clinker and supplementary cementitious materials (SCMs) fractions, in terms of hydration process and strength contribution ratio, was characterized. The results show that blast furnace slag and steel slag should preferably be arranged in fine fractions due to their desirable hydration processes and high strength contribution ratios. Cement clinker should be positioned in intermediate fraction (8–24 μm) due to its proper hydration process. Replacement of cement clinker by SCMs with low activity or inert fillers in coarse fractions was also suggested, because coarse cement clinker fractions gave very low hydration degrees and little strength contribution. Both early and late properties of gap-graded blended cements prepared can be comparable with or higher than those of Portland cement, indicating both cement clinker and SCMs were used more efficiently. These blended cements also give additional cost savings and reduced environmental impact.

1. Introduction

Portland cement is not an environmental friendly material because its manufacture creates large quantities of greenhouse gas emissions; and it also consumes a large amount of natural resources and energy. As cement industry is being adapted to more stringent environmental regulations, utilization of industrial by-products as supplementary cementitious materials (SCMs) in blended cement manufacture has been noted for engineering, ecological and economic benefits [1]. However, one shortcoming of blended cements that has not yet been completely solved is their relatively low early strengths [2].

Chemical activation [3–5] and/or ultra-fine grinding [6–8] are usually applied to improve the early strengths of blended cements, which usually lead to increased costs or difficulties in engineering practice. It can be concluded that the incentive of these methods is to improve the pozzolanic activities of SCMs. To maximize the properties of blended cements and the substitution level of SCMs, cement clinker and SCMs are expected to be arranged in corresponding size fractions according to their hydraulic or pozzolanic activities. In previous study, a gap-graded particle size distribution (PSD) was proposed to achieve high packing density of blended cement paste, then gap-graded blended cements were prepared through arranging blast furnace slag (BFS) in fine fraction (<8 μm), cement clinker in intermediate fraction (8–32 μm) and other SCMs in coarse fraction (>32 μm). It is also proved that the properties of the gap-graded blended cements can be comparable with those of Portland cement [9].

To specify how to arrange cement clinker and SCMs in the gap-graded PSD more efficiently, the authors, in the present study, have further classified the cement particles into five different fractions. According to the Horsfield packing model [10] and traditional practice, the (volume median) diameters of particles of five filling grades were selected as 3 μm, 6 μm, 16 μm, 32 μm, 63 μm for easy operation, then cement particles were divided into five fractions, i.e. <4 μm, 4–8 μm, 8–24 μm, 24–45 μm, and >45 μm [11]. The PSD of each fraction should be as narrow as possible, while the overall PSD of the blended cement should be wide and as close as possible to the Fuller distribution curve (Fig. 1). The target parameters of the gap-graded PSD are summarized in Table 1.

Hydration degree and strength contribution ratio of cementitious material fractions were characterized in the present study, then high performance gap-graded blended cements with only 25% clinker content were obtained through arranging SCMs and clinker in the gap-graded PSD according to their hydration processes and strength contribution ratios. The results will be very useful to prepare high performance blended cements with low cement clinker content and utilize SCMs and cement clinker more efficiently both in cement manufacturing and concrete making.

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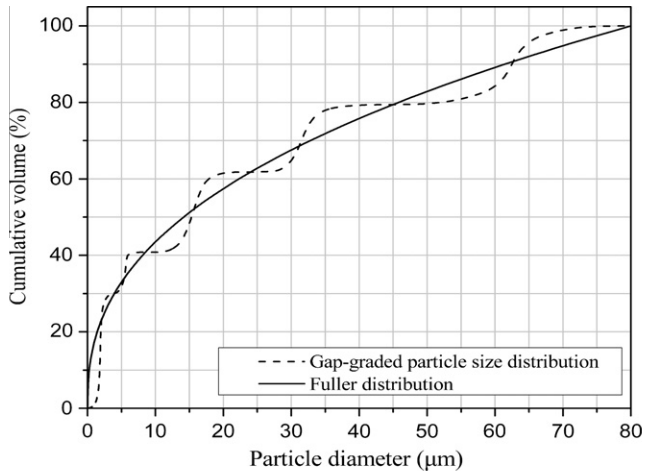

Fig. 1. Comparison of gap-graded particle size distribution and Fuller distribution.

Table 1
Parameters of the target gap-graded particle size distribution.

Filling grade	Fifth	Fourth	Third	Second	First
Median diameter of each grade (μm)	3	6	16	32	63
Diameter range (μm)	<4	4–8	8–24	24–45	>45
Incremental volume (%)	25	11	25	19	20
Cumulative volume (%)	25	36	61	80	100

2. Experimental

2.1. Raw materials and classification of cementitious materials

A Portland cement clinker, BFS, low-calcium fly ash (a class F fly ash according to ASTM C 618 [12]), steel slag (a by-product of steel converter) and quartz sand (as an inert filler) were ground and then separated using a laboratory air classifier (based on the gravitational/sedimentation principle). The chemical compositions of raw materials used are given in Table 2. By changing operational parameters of the classifier, each kind of raw material was separated into five fractions (<4 μm, 4–8 μm, 8–24 μm, 24–45 μm, >45 μm) according to the gap-graded PSD (see Table 1). Only small deviation in chemical composition with size fraction was observed for Portland cement clinker, fly ash and steel slag [9], therefore the effects of deviation in chemical composition on the properties of cementitious material fractions were neglected in the present study. That is to say, the influences of particle size on the properties of cementitious material fractions were mainly discussed. The mineral composition of the Portland cement clinker measured by quantitative X-ray diffraction [13] is given in Table 3.

The actual PSDs of the five cement clinker fractions, 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. 2, and the PSDs of SCMs and quartz sand fractions are similar to those of corresponding cement clinker fractions. The PSD of each fraction roughly meets the requirements of the gap-graded PSD, even though there is certain overlap among each fraction due to low classification efficiency of the classifier used.

As close packing theory is based on volume proportion, blended cements were proportioned by volume for easy operation (if mass proportion was used, the densities of SCMs in each fraction should be taken into account). Gap-graded blended cements were prepared by mixing each cementitious materials fractions and gypsum dihydrate homogenously.

2.2. Testing methods

2.2.1. Packing density of cement pastes

Maximum solid volume concentration is used to characterize the packing density of cement pastes [14]. The method is specified in our previous study [9]. Meanwhile water requirements for normal consistency of blended cements were also determined according to EN 196-3 [15].

2.2.2. Hydration degree of cement clinker and SCMs

Hydration degree of each cement clinker and SCMs fraction was tested at certain fluidity. Hydration degree of cement clinker paste of normal consistency was investigated by testing non-evaporable water content [16]. While hydration degrees of SCMs in simulative pore solution (supersaturated $Ca(OH)_2$–0.2 mol/L (M) NaOH solution [17]) were followed. 90% BFS or fly ash fractions (by mass) and 10% CaO were mixed with 0.2 M NaOH solution into a paste of normal consistency. Hydration degree of BFS was investigated by ethylene diamine tetraacetic acid disodium salt (EDTA) selective dissolving method [18], and reaction degree of fly ash was tested by HCl selective dissolving method [19]. Steel slag was mixed with 0.2 M NaOH solution into a paste of normal consistency, and then hydration degree of steel slag paste was measured by testing non-evaporable water content. It should be noted that the non-evaporable water content of 1 g completely hydrated steel slag tested in the present experiment was 0.22 g.

2.2.3. Heat evolution of cement pastes

The heat evolution of cement pastes made at a water to cementitious material mass ratio of 0.5 was followed for 72 h at 25 °C using a TAM-Air isothermal calorimeter according to ASTM C 1702-09 [20].

2.2.4. Microstructure and hydration products of hardened cement pastes

Cement pastes made at normal consistency (water requirement for normal consistency was measured as outlined in Section 2.2.1 and will be given in Section 3.4.2) were cast into plastic bags and sealed before placed in a 20 ± 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, then

Table 2
Chemical compositions of quartz sand, Portland cement clinker, BFS, low calcium fly ash and steel slag used.

Material	Chemical composition (%)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI
Quartz sand	99.16	0.36	0.12	0.18	0.06	0.02	0.01	0.02	0.02
Portland cement clinker	21.60	4.35	2.95	63.81	1.76	0.51	0.16	2.06	1.19
Blast furnace slag	35.22	12.15	0.25	37.08	11.25	0.49	0.25	1.19	−0.36
Low calcium fly ash	45.43	24.36	6.70	7.53	1.51	1.23	0.36	1.03	7.88
Steel slag	14.84	3.59	24.14	39.14	9.33	0.05	0.05	0.16	5.91

Note: LOI, loss on ignition.

Table 3
Mineral composition of the Portland cement clinker used in the experiment.

Material	Mineral composition (%)				
	C_3S	C_2S	C_3A	C_4AF	f-CaO
Portland cement clinker	63.5 ± 1.3	15.4 ± 0.6	7.2 ± 0.3	8.6 ± 0.4	1.5 ± 0.1

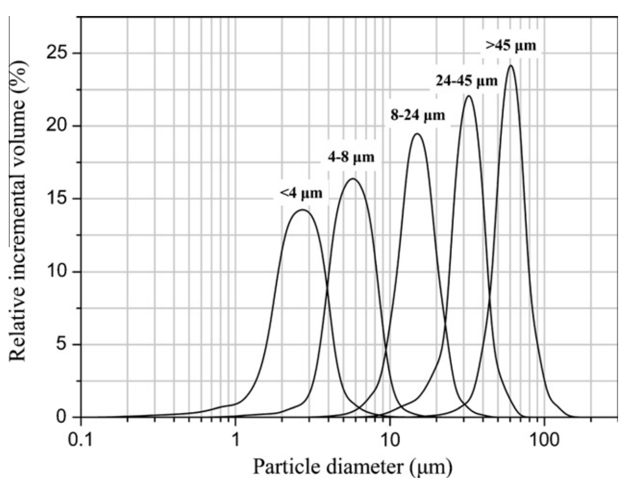

Fig. 2. Particle size distributions of classified Portland cement clinker fractions.

vacuum-oven-dried at 60 °C for at least 48 h. Their microstructures were observed using a scanning electric microscope (SEM, Nano 430, 10 kV), hydration products and un-hydrated cementitious materials were characterized by X-ray diffraction (XRD) under the conditions of 40 kV, 15 mA, Cu Kα.

2.2.5. Compressive and flexural strengths of cement mortars

40 × 40 × 160 mm mortar prisms were prepared at a water:cement:standard sand [21] mass ratio of 0.5:1:3. After curing at 20 ± 1 °C and 90% relative humidity (R.H.) for 24 h, the specimens were demoulded and cured in lime-saturated water at 20 ± 1 °C, followed by strength tests according to EN 196-1 [22].

3. Results and discussion

3.1. Hydration processes of cementitious materials fractions

Expansion of solid phases was observed during the hydration of cementitious materials, therefore the hydration degrees of cementitious materials at different ages can be seen as an index of ability of filling pores. However, rapid hydration of fine particles in the first few hours usually leads to high water requirement. Thus it is expected that cementitious materials present a relatively low hydration degree and high hydration degree in the first few hours and late ages, respectively. Hydration degrees of each cementitious materials fraction at 1 h (mixing period of cement mortar or concrete), 3 days and 28 days were characterized as shown in Table 4.

Fine cement clinker fractions (<4 μm and 4–8 μm) showed very high 1-h hydration degree (19.4% and 7.9%), which resulted in a very high water requirement [16]. The 8–24 μm cement clinker fraction gave relatively low 1-h hydration degree and high hydration degree for 3-day and 28-day of hydration, while coarse cement clinker fractions (24–45 μm and >45 μm) presented very low hydration degrees at all tested ages.

The fine BFS fractions (<4 μm and 4–8 μm) gave desirable 1-h hydration degree and high 3-day and 28-day hydration degrees. For instance, the 3-day and 28-day hydration degrees of the <4 μm BFS fraction can be as high as 51.8% and 96.5%, respectively. In contrast, both early and late hydration degrees of other BFS fractions were very low.

Hydration degrees of all fly ash fractions were much lower than those of corresponding BFS fractions, and the difference between hydration degrees of fly ash fractions (both fine and coarse) was much smaller compared with that of BFS fractions, suggesting that the enhancement of pozzolanic properties of low-calcium fly ash is very limited through ultra-fine grinding.

It is generally accepted that steel slags have very low hydraulic activity, although they often contain 50% or more C_3S and C_2S. In our results, the finest steel slag (<4 μm) fraction presented similar hydration degrees to corresponding (<4 μm) BFS fraction at all ages, indicating significant improvement of hydraulic activity of steel slag due to large specific surface area. The 4–8 μm steel slag fraction had a low 1-h hydration degree (1.1%) and a relatively high 28-day hydration degree (54.6%). Hydration degrees of other steel slag fractions can be neglected, especially at early ages. It can be concluded that the hydration processes of steel slag fractions present significant differences depending on their size.

3.2. Strength contribution ratios of SCMs

3.2.1. Basic hypothesis

The strength of each Portland or blended cement is treated as the sum of the strength contributions of all its fractions; other factors (e.g. interactions) influencing the strength are neglected in this approximate treatment. The strengths of cements with various SCMs fractions can be calculated by:

$$S = (R_i \cdot V_i + \cdots + R_j \cdot V_j) \cdot S_0 \tag{1}$$

where S_0 is the strength of Portland cement; S is the strength of a blended cement with the same overall PSD as the Portland cement, R_i and R_j are the strength contribution ratios of fraction i and j, V_i and V_j are the volume contents of the fraction i and j, respectively.

The strength contribution ratio of each Portland cement fraction is designated as 100% regardless of its PSD, and the strength contribution ratio of SCMs fraction is defined as the ratio of its strength contribution to that of corresponding cement clinker fraction. If only one cement clinker fraction is replaced by a corresponding SCMs fraction, the strength contribution ratio of the SCMs fraction can be calculated simply by:

$$R = \left(\frac{S}{S_0} + V - 1\right) \Big/ V \tag{2}$$

where R is the strength contribution ratio of the SCMs fraction and V is its volume content.

If R is negative, it means the replacement of cement clinker fraction by corresponding SCMs fraction reduces the strength under the conditions tested (mortar composition, curing time, etc.). Conversely, if R is positive, the strength is increased. When R is higher than 100%, it means that the SCMs fraction tested gives a higher strength contribution than corresponding clinker fraction. Although this ratio is not an absolute constant (it depends on the conditions of the test used to measure it), the strength contribution ratio of a SCMs fraction can be used as quantitative measurement of its contribution to overall cement performance.

Table 4
Hydration degrees of classified ground cement clinker, BFS, low calcium fly ash and steel slag fractions (%).

Fraction (μm)	Cement clinker			BFS			Low calcium fly ash			Steel slag		
	1 h	3 days	28 days	1 h	3 days	28 days	1 h	3 days	28 days	1 h	3 days	28 days
<4	19.4	97.18	99.8	3.1	51.8	96.5	1.1	13.3	24.1	2.9	48.6	95.2
4–8	7.9	80.5	98.6	1.3	25.5	92.3	0.3	5.4	17.6	1.1	24.6	54.6
8–24	3.2	43.7	86.9	0.3	9.1	47.2	0.1	1.0	5.3	0.2	3.7	17.7
24–45	1.4	20.6	39.4	0.2	4.8	20.3	0.1	0.5	3.2	0.1	1.3	11.3
45–80	0.4	10.2	19.6	0.1	0.8	5.8	0.0	0.2	2.1	0.1	0.4	6.4

It is generally accepted that cement clinker particles in the range of 3–30 μm make a dominant contribution to the strengths of Portland and blended cements [23], thus the 8–24 μm fraction was kept as clinker in all of gap-graded blended cements. Blended cements were prepared by mixing one SCMs (or inert filler) fraction and the rest of the cement clinker fractions homogeneously. The mix proportions of the single-size-fraction substitution blended cements are shown in Table 5. The final PSDs of these blended cements showed only slight differences (see Fig. 3), therefore it is regarded that these gap-graded blended cements have same PSD.

3.2.2. Strength contribution ratios of SCMs fractions

The mortar test results of single-size-fraction substitution blended cements are listed in Table 5, and the strength contribution ratios of SCMs calculated using Eq. (2) are given in Table 6.

The fine quartz sand fraction (<4 μm) showed positive 3-day and 28-day strength contribution ratios due to grain size refinement. In contrast, other fractions had negative 3-day strength contribution ratios (especially for the 4–8 μm fraction) and nearly no contribution to 28-day strengths of blended cement.

The fine BFS fractions (<4 μm and 4–8 μm) gave very high 3-day compressive strength contribution ratios, (especially the finest fraction), while coarse BFS fractions (24–45 μm and >45 μm) presented nearly no contribution to 3-day compressive strengths. In contrast, the 28-day compressive strength contribution ratios of all BFS fractions were greater than 100%. Similar trends were also observed for the flexural strength contribution ratios. The results are consistent with Y.J. Zhang's findings [24], which indicated that the 5–10 μm BFS fraction had the maximum positive effect on 7-day strengths development, and the 10–20 μm fraction had the maximum positive effect on 28-day strengths development.

Replacement of any cement clinker fraction by the corresponding low-calcium fly ash fraction led to significant reduction in 3-day compressive strengths, especially for the 4–8 μm fraction. Only the finest fly ash fraction had an acceptable 28-day compressive strength contribution ratio (>80%), the other fly ash fractions gave almost no contribution to 28-day strengths.

The addition of steel slag to blended cements generally reduces both early and late strengths of blended cement. That is to say, steel slag shows very low activity index. In our results, both 3-day and 28-day compressive strength contribution ratios of the finest steel slag fraction were higher than 100%, indicating that fine steel slag fraction (<4 μm) can have a better effect on strength development than the corresponding cement clinker fraction. In contrast, the other steel slag fractions showed relatively low strength contribution ratios.

3.2.3. Strength contribution ratio due to hydraulic (pozzolanic) activity or increased packing density

Quartz sand is believed to only have influence on packing density, thus the strength contribution ratio differences between individual SCMs and quartz sand fractions can be attributed to the hydraulic or pozzolanic activity of the SCMs. Finest quartz sand fraction has positive strength contribution ratio, indicating grain size refinement of fine particle has certain positive contribution to the strengths of blended cement. However, strength contribution ratio due to grain size refinement diminishes as particle size increases. In addition, all fly ash fractions gave 3-day strength contribution ratios even lower than those of quartz sand due to high un-burnt carbon content (Table 2), suggesting that the surface properties also influence the strength contribution of SCMs.

It can be inferred that the strength contribution ratios due to hydraulic activity decreases sharply with the increase of particle

Table 5
Mix proportions of the single-size-fraction substitution blended cements and their mortar strengths.

Fraction (μm)	<4	4–8	8–24	24–45	45–80	Flexural strength (MPa)		Compressive strength (MPa)	
Content (%)	25	11	25	19	20	3 days	28 days	3 days	28 days
CCCCC	C	C	**C**	C	C	7.7	9.2	31.1	48.0
QCCCC	**Q**	C	**C**	C	C	6.5	8.0	26.5	42.9
CQCCC	C	**Q**		C	C	6.1	8.3	24.4	42.8
CCCQC	C	C		**Q**	C	5.2	7.5	23.4	37.9
CCCCQ	C	C		C	**Q**	5.3	7.7	24.9	38.3
BCCCC	**B**	C	**C**	C	C	8.6	11.0	38.2	53.4
CBCCC	C	**B**		C	C	7.6	9.3	32.1	51.0
CCCBC	C	C		**B**	C	5.4	9.6	24.7	52.0
CCCCB	C	C		C	**B**	5.9	9.3	25.7	51.2
FCCCC	**F**	C	**C**	C	C	4.9	9.8	21.5	46.9
CFCCC	C	**F**		C	C	5.0	7.9	22.5	43.5
CCCFC	C	C		**F**	C	4.7	7.5	20.6	38.3
CCCCF	C	C		C	**F**	4.8	7.4	23.0	40.3
SCCCC	**S**	C	**C**	C	C	7.4	9.0	33.9	48.9
CSCCC	C	**S**		C	C	6.0	8.1	25.7	45.0
CCCSC	C	C		**S**	C	5.3	7.6	24.2	42.9
CCCCS	C	C		C	**S**	5.4	7.8	25.1	39.3

Note: 5% of gypsum dihydrate by mass of cementitious material was added for all the cements listed in this table; Q, C, B, F and S represent quartz sand, cement clinker, blast furnace slag, low calcium fly ash and steel slag, respectively.

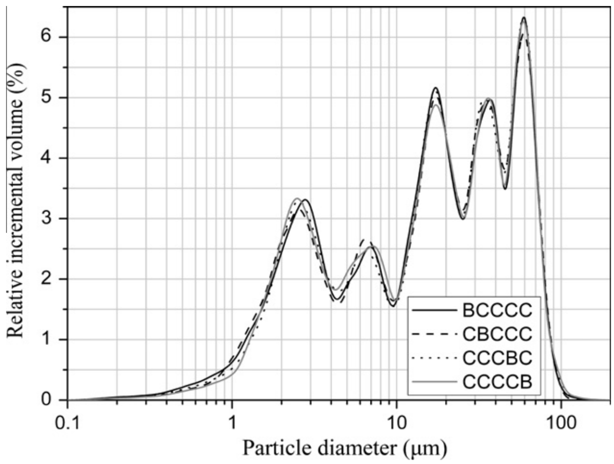

Fig. 3. Particle size distributions of four BFS incorporated gap-graded blended cements.

size, especially for early ages. For instance, the 3 days strength contribution ratios of the two fine fractions (<4 μm and 4–8 μm) of SCMs are largely dependent on their hydraulic activity. The late ages strength contribution ratios of all SCMs fractions are mainly dominated by their hydraulic activity. It should be noted that the 28 days strength contribution ratios of the finest BFS fraction is not the highest due to its very high water requirement. Similar trend was also observed for Portland cement fractions [16].

3.3. Improvement of the cementitious efficiency of blended cements

Compared with fine cement clinker fractions (<4 μm and 4–8 μm), fine BFS and steel slag fractions have desirable hydration degrees and higher strength contribution ratios at all tested ages. Hydration of very fine SCMs particles during mixing process (such as 1 h) is small in comparison to that of very fine cement clinker particles, and replacement of cement clinker by SCMs with high activity in the fine fractions (<4 μm and 4–8 μm) results not only in a reduction in water requirement, but also in adequate hydraulic activity of the SCMs due to their large specific surface area. Thus cement clinker can be replaced by BFS or steel slag in fine fractions.

8–24 μm cement clinker fraction has relatively low 1-h hydration degree (3.2%) and high 3-day and 28-day hydration degrees (43.7% and 86.9% respectively). In contrast, SCMs fractions with 8–24 μm show very low hydration degrees at all ages. Thus cement clinker should be positioned in the 8–24 μm fraction and is anticipated to play a dominant contribution in the strength development of gap-graded blended cements. The conclusion has been proved by Celik [25] and Zhang et al. [16].

Whatever hydraulic activity that cementitious materials fractions have, coarse particles (>24 μm) mainly give a "filler effect" and don't make much contribution to the strength development of hardened cement paste [26]. BFS is preferred to be arranged in coarse fractions (24–45 μm and >45 μm), because it will not result in 28-day strengths loss. Although the replacement of cement clinker by other SCMs in coarse fractions reduces the strengths of blended cements slightly, SCMs with low activity (steel slag, low-calcium fly ash or natural pozzolans) or inert fillers (such as quartz sand, and limestone powder) are also recommended, which can give additional cost savings as well as a reduced environmental impact.

3.4. Fundamental properties of gap-graded blended cements with low clinker content

To utilize cement clinker and SCMs more efficiently and maximize the strengths of gap-graded blended cements, SCMs with high activity (such as BFS), cement clinker, and SCMs with low activity (low-calcium fly ash and steel slag) were arranged in the fine (<4 μm and 4–8 μm), intermediate (8–24 μm) and coarse fractions (24–45 μm and >45 μm), respectively.

Low-clinker gap-graded blended cements with the proportions shown in Table 7 were prepared by mixing cement clinker fraction and SCMs fractions homogeneously. A Portland cement and a reference cement consisting of 36% BFS, 25% cement clinker and 39% fly ash (gypsum dehydrate is added additionally) were prepared by co-grinding. The Blaine specific surface areas of these two cements were controlled in the range of 350–360 m^2/kg, which was close to those of the gap-graded blended cements.

Table 8 shows that the low-clinker gap-graded blended cements had much lower water requirements for normal consistency than the reference blended cement. Because the coarse fly ash fractions contained much un-burnt carbon and porous particles, which resulted in a relatively high water requirement of BBCFF cement paste. Gap-graded blended cements without fly ash showed water requirements for normal consistency only slightly higher than that of the Portland cement. The Portland cement had the lowest water requirement for normal consistency, because the amount of very fine particles (<4 μm) of Portland cement was much lower than that of the gap-graded blended cements prepared, i.e. about 10% less than that of the gap-graded blended cements (25%).

Table 8 also shows that the maximum solid volume concentrations of the Portland cement and reference cement pastes were 49.12% and 45.40%, respectively, while the gap-graded blended cement pastes gave much higher maximum solid volume concentrations. For example, the maximum solid volume concentration of BBCFF cement paste was as high as 55.62%, i.e. 10.22% higher than that of reference cement. The results prove the gap-graded blended cement pastes can give significantly higher packing density than blended cements prepared by co-grinding.Reference blended cement presented very low rate of heat evolution in the first 72 h as shown in Fig. 4, otherwise, the calorimetric curve of reference blended cement showed similar shape with that of Portland

Table 6
Strength contribution ratios of classified ground quartz sand, BFS, low calcium fly ash and steel slag fractions (%).

Fraction (μm)	Quartz sand				BFS				Low calcium fly ash				Steel slag			
	Compressive strength		Flexural strength		Compressive strength		Flexural strength		Compressive strength		Flexural strength		Compressive strength		Flexural strength	
	3 days	28 days	3 days	28 days	3 days	28 days	3 days	28 days	3 days	28 days	3 days	28 days	3 days	28 days	3 days	28 days
<4	40.8	57.5	37.7	47.8	191.3	145.0	146.8	178.3	−23.5	90.8	−45.5	126.1	136.0	107.5	84.4	91.3
4–8	−95.8	1.5	−88.9	11.1	129.2	156.8	88.2	109.9	−151.4	14.8	−218.8	−28.5	−57.8	43.2	−100.7	−8.7
24–45	−30.3	−10.7	−70.9	2.7	−8.3	143.9	−57.2	122.9	−77.7	−6.4	−105.1	2.7	−16.8	44.1	−64.0	8.5
45–80	−4.5	−1.0	−55.8	18.5	13.2	133.3	−16.9	105.4	−30.2	19.8	−88.3	2.2	3.5	9.4	−49.4	23.9

Table 7
Mix proportions of the low-clinker gap-graded blended cements.

Fraction (μm)	<4	4–8	8–24	24–45	45–80
Content (%)	25	11	25	19	20
BBCFF	B	B	**C**	F	F
BBCSS	B	B		S	S
BBCBB	B	B		B	B
SBCFF	S	B		F	F
BFCFF	B	F		F	F
BSCFF	B	S		F	F
Portland cement	100% cement clinker				
Reference cement	36% BFS + 25% cement clinker + 39% fly ash				

Note: 5% of gypsum dihydrate by mass percent of cementitious material was added for all the cements in this table; C, B, F and S represent cement clinker, blast furnace slag, low calcium fly ash and steel slag, respectively.

Table 8
Maximum solid volume concentrations and water requirements for normal consistency of gap-graded blended cement pastes.

Cement	BBCFF	BBCSS	BBCBB	SBCFF	BFCFF	BSCFF	Portland cement	Reference cement
Specific density (g/cm^3)	2.816	3.211	2.824	2.841	2.834	2.928	3.150	2.870
Setting time (min)								
Initial	135	120	110	150	140	143	95	185
Finial	190	185	176	210	195	205	151	256
Maximum wet density (g/cm^3)	2.010	2.247	2.028	2.010	1.981	2.045	2.056	1.849
Maximum solid volume concentration (%)	55.62	56.42	56.37	54.85	53.48	54.20	49.12	45.40
Water requirement for normal consistency	0.334	0.316	0.317	0.332	0.339	0.338	0.305	0.356

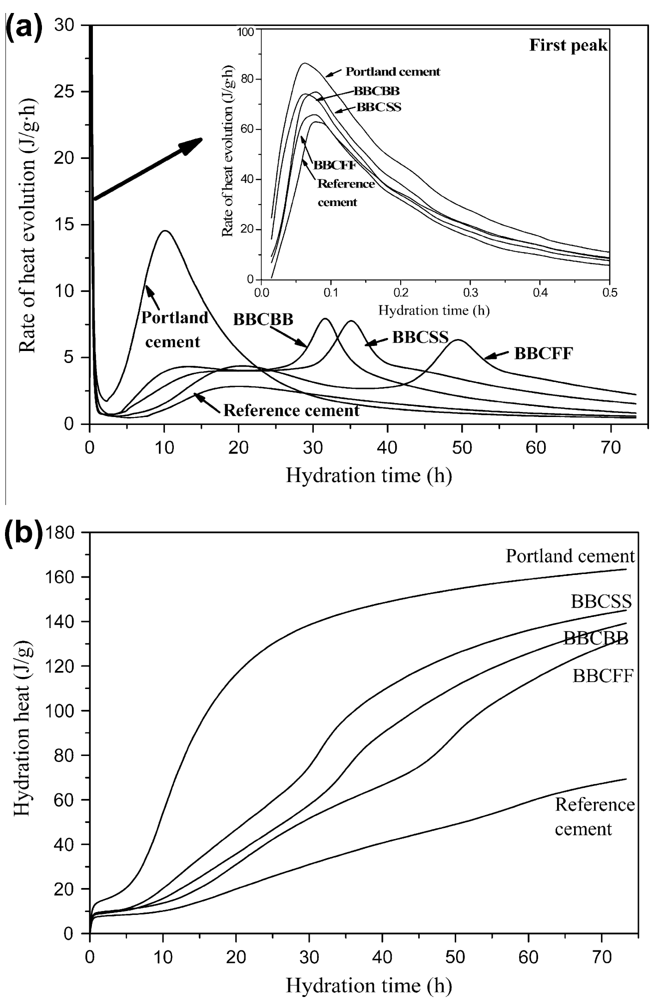

Fig. 4. Heat evolution of gap-graded blended cement pastes at water to cementitious material mass ratio of 0.5. (a) Rate of heat evolution; (b) cumulative hydration heat.

cement. For calorimetric curves of the gap-graded blended cement pastes, the first peak (around 0.1 h) and the second peak (5–20 h), both correspond to the hydration of cement clinker, were much lower than those of Portland cement due to the low clinker content. More important, an additional peak (occurring at 30–50 h) was observed and can be attributed to the hydration of fine BFS particles. Clearly, the hydration of fine BFS particles in the gap-graded blended cements played much more significant role than that in reference cement produced by co-grinding similar ingredients. As a result, the cumulative heat of hydration of the gap-graded blended cements tested here was twice that of reference cement and about 80% of that of the Portland cement.

Fig. 5a–c showed the relatively low amount of hydration products in the reference blended cement paste at 1, 3 and 28 days, in comparison to the Portland cement paste at the same ages (Fig. 5d–f). Cement clinker particles coarser than 30 μm had only hydrated superficially after 3 days, implying that this part of costly cement clinker exhibits low cementitious efficiency (in effect being wasted) and make little contribution to strength development. Gap-graded BBCFF blended cement pastes showed significantly denser microstructure than reference cement paste and apparently even slightly denser than Portland cement paste at all ages (Fig. 5g–i). In addition, in gap-graded blended cements the hydration products appeared to bond better with the un-hydrated particles.

XRD patterns of hardened cement pastes cured for 28 days were given in Fig. 6. Diffraction patterns of residual C_3S and C_2S were very significant in Portland cement paste, implying certain amount of cement clinker remains un-hydrated after 28 days curing. Small amount of C_3S and C_2S can also be identified in reference blended cement. While nearly no residual C_3S and C_2S and lower amount of $Ca(OH)_2$ were found in the BBCFF cement paste cured for 28 days, suggesting that cement clinker is more efficiently used and more significant pozzolanic reaction takes place in the gap-graded blended cement pastes than in reference blended cement paste.

Both 3-day and 28-day compressive strengths of the low-clinker gap-graded blended cements increased significantly relative to the reference cement and can be comparable with or higher than those of Portland cement (Table 9). All of the low-clinker gap-graded blended cements gave much higher flexural strengths

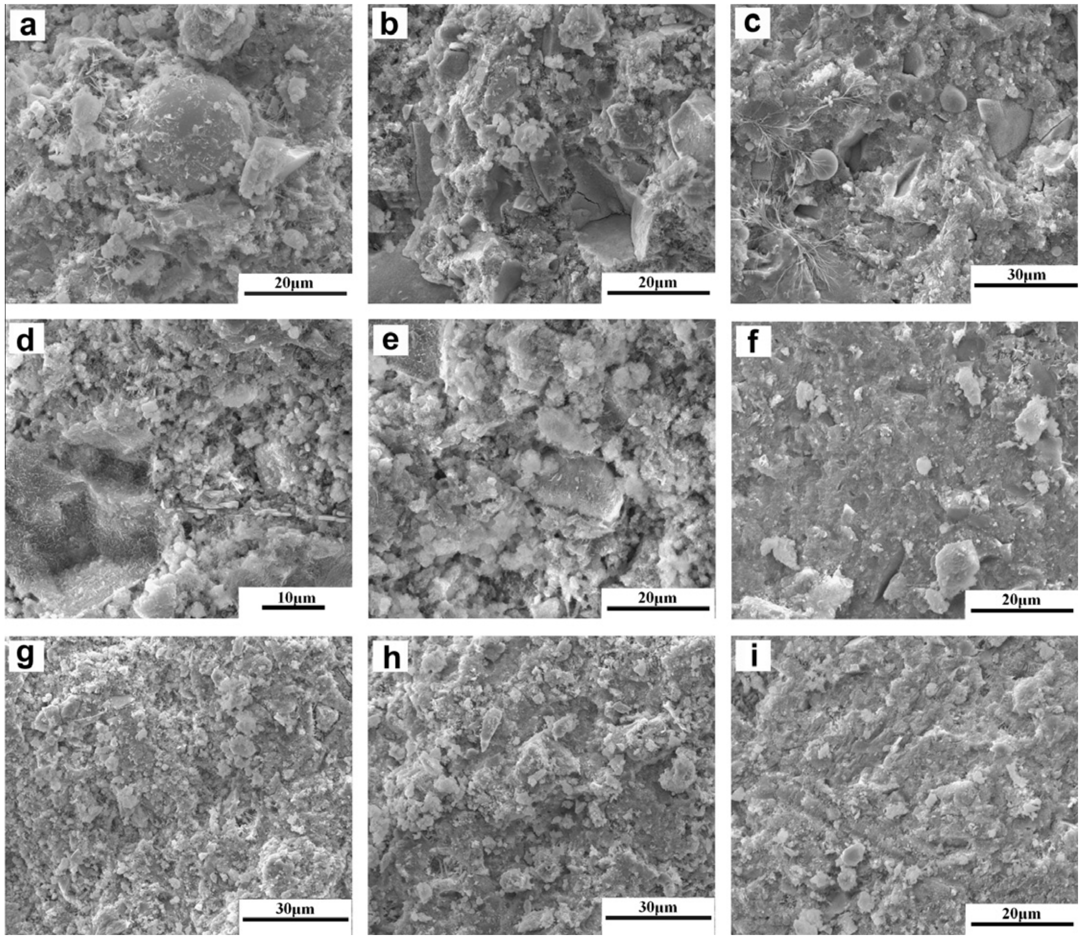

Fig. 5. SEM images of hardened cement pastes. (a–c) Reference cement pastes cured for 1, 3 and 28 days, respectively; (d–f) Portland cement pastes cured for 1, 3 and 28 days, respectively; (g–i) BBCFF blended cement pastes cured for 1, 3 and 28 days, respectively.

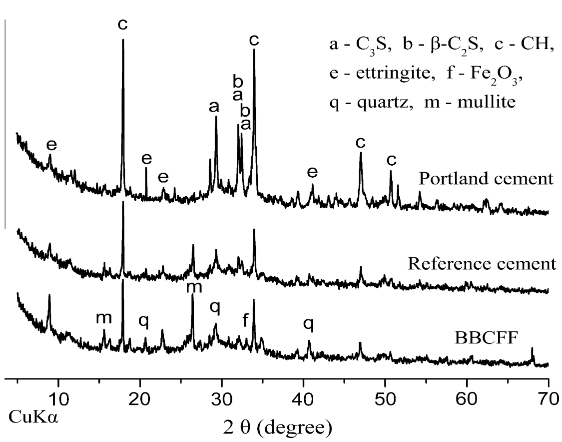

Fig. 6. XRD patterns of hardened cement pastes cured for 28 days.

than the reference cement or even Portland cement. For instance, the 28-day flexural strength of BBCBB cement was over 12 MPa.

4. Discussion

4.1. Efficiency comparison of reference cement, Portland cement and gap-graded blended cements

Both fine and coarse Portland cement fractions have undesirable strength contribution, and about 30% of cement clinker (mainly coarse clinker particles) remained un-hydrated after 28 days curing [16]. Although with low clinker content, reference cement paste cured for 28 days also contains certain un-hydrated clinker, and pozzolanic reaction of SCMs is very slight, especially for early ages. Obviously, both Portland cement and reference cement present lower cementitious efficiency compared with gap-graded blended cements.

The properties of gap-graded blended cements with three fractions (<8 μm, 8–32 μm and >32 μm) has been closely investigated [9]. Compared with gap-graded blended cements with three fractions (for example BCB), gap-graded blended cements with five fractions (for instance BBCBB prepared in this study) presented higher packing density and higher rate of heat evolution. For instance, maximum solid volume concentration of BBCBB cement paste is 56.37%, while that of BCB cement paste is 52.64%. The third

Table 9
Compressive and flexural strengths of gap-graded blended cement mortars.

Cement	Compressive strength (MPa)		Flexural strength (MPa)	
	3 days	28 days	3 days	28 days
BBCFF	24.1 ± 0.4	43.8 ± 0.6	6.2 ± 0.2	10.0 ± 0.4
BBCSS	25.0 ± 0.3	47.1 ± 0.6	5.9 ± 0.2	10.8 ± 0.4
BBCBB	24.4 ± 0.3	49.2 ± 0.4	6.8 ± 0.2	12.2 ± 0.4
SBCFF	23.8 ± 0.4	39.3 ± 0.5	5.3 ± 0.3	8.6 ± 0.4
BFCFF	20.2 ± 0.5	35.5 ± 0.7	5.6 ± 0.4	8.5 ± 0.5
BSCFF	21.3 ± 0.4	38.1 ± 0.6	5.9 ± 0.2	8.6 ± 0.5
Portland cement	23.5 ± 0.5	45.0 ± 0.6	7.7 ± 0.4	9.2 ± 0.5
Reference cement	11.32 ± 0.4	29.6 ± 0.6	3.3 ± 0.2	7.1 ± 0.4

heat evolution peak of BBCBB is with a value of about 7.0 J/g h and occurs at 30–50 h, while that of BCB is with a value lower than 5.0 J/g h and occurs at 55–70 h. The total heat of hydration of BBCBB is about 140 J/g, and changes to about 110 J/g for BCB cement. As a result, the 28-day flexural and compressive strengths of BBCBB are 12.2 MPa and 49.2 MPa, which are much higher than those of BCB cement (10.0 MPa and 43.1 MPa).

The above discussion shows that both cement clinker and SCMs are used more efficiently in gap-graded blended cements with five fractions than in gap-graded blended cements with three fractions, and that the former gives superior properties than the latter.

4.2. Strength improvement mechanism of gap-graded blended cements

The experimental results prove that gap-graded blended cement (both with three fractions and five fractions) pastes have higher packing density than reference blended cement and Portland cement pastes, that is to say, distance among particles in gap-graded blended cement pastes become shorter and fewer amounts of hydration products are needed to achieve dense microstructure. Meanwhile, the hydraulic (or pozzolanic) activity of fine SCMs increases significantly due to their large specific surface area. $Ca(OH)_2$ reacts with fine SCMs to form more C–S–H gel which gradually fills in the larger pores. Thus the microstructure of gap-graded blended cement pastes is much more homogeneous and denser than that of reference cement paste or even Portland cement paste. This is why both the 3-day and 28-day compressive strengths of gap-graded blended cements with only 25% cement clinker by mass can be comparable with or higher than that of Portland cement, especially when a fairly reactive hydraulic SCMs (such as BFS) is used in the fine (<4 μm and 4–8 μm) fraction.

5. Conclusions

The main conclusions that can be drawn from this experimental study are summarized as follows:

(a) BFS and steel slag show more desirable hydration processes and higher strength contribution ratios than cement clinker in fine fractions (<4 μm and 4–8 μm), therefore cement clinker can be replaced by BFS or steel slag in the fine fractions of blended cement.
(b) The 8–24 μm cement clinker fraction has proper hydration process, while SCMs fractions with 8–24 μm present very low hydration degrees. Thus cement clinker should preferably be positioned in the 8–24 μm fraction.
(c) Both cement clinker and SCMs show very low hydration degrees in coarse fractions (24–45 μm and >45 μm). Replacement of cement clinker by SCMs with low activity or inert fillers in coarse fractions is suggested, although it will slightly reduce the strengths of blended cement.
(d) Both early and late properties of low-clinker gap-graded blended cements can be comparable with or higher than those of Portland cement due to homogeneous, dense microstructure, indicating both cement clinker and SCMs are used more efficiently. These blended cements also give additional cost savings as well as a reduced environmental impact.

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