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Characterization of mortars from belite-rich clinkers produced from inorganic wastes

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ABSTRACT

The purpose of this study was to use inorganic wastes to totally replace traditional raw materials for the production of belite-rich clinkers and to investigate the hydration characteristics of the resulting mortars. The produced clinkers were rich in β-dicalcium silicate, and mixed with ordinary Portland cement at various proportions to form blended cements. The hydration of the cement pastes was slowed down by increasing the fraction of belite-rich clinkers. However, the blended cement mortars had comparable compressive strength to the commercial ordinary Portland cement mortar at later curing ages. The results indicate that the blended cements containing up to 40% belite-rich clinkers can still satisfy the compressive strength requirements for Type I Portland cements. The high fraction of belite-rich clinkers in the blended cements produces pastes with longer linear polysilicate anions in the calcium silicate hydrates, which could contribute to the high later-age strength of these blended cement paste mortars.

1. Introduction

Recent challenges for the cement manufacturing industry are sources of raw materials and the issues of air pollution (particularly carbon dioxide emissions). In 2008, the annual amount of world cement production rose to 2.83 Gt [1], and approximately 5.09 Gt of raw materials were required to produce this, using the multiplier of 1.8 that was reported by van Oss and Padovani [2]. The cement raw materials mainly come from natural quarries of limestone, clay, sandstone, and ironstone, but these finite deposits will inevitably be exhausted someday. Accordingly, many researchers have studied the feasibility and applicability of reusing various waste materials, e.g. rice husk ash [3], fresh-water and sewage sludges [4,5], metallurgical slags [6,7], and municipal solid waste incineration fly ash [8], in the production of cement clinkers, and it has been proposed that these wastes have high potential for being alternative raw materials.

In terms of air pollution, although most of the exhaust pollutants from kilns (such as dust, sulfur oxide, nitrogen oxide, and dioxins) can be removed with air pollution control devices, the carbon dioxide emissions of the cement industry are still a serious concern. Some studies have suggested that the cement industry contributes about 5% to global anthropogenic CO_2 emissions [9,10]. The decarbonation of raw materials (mostly for limestone) and the combustion of fuels, which approximately account for 50% and 43% of the CO_2 emissions of cement manufacturing, respectively, are the major emission sources, while electricity use indirectly contributes about 7% [2]. Lawrence [11] reviewed various low-energy cements that are beneficial to reduce CO_2 emissions and indicated that reducing the CaO content of clinkers can result in belite (Ca_2SiO_4, C_2S) based clinkers rather than regular alite (Ca_3SiO_5, C_3S) based ones, and this leads to the reduction of CO_2 emissions both from decarbonation of raw materials (less limestone required) and the combustion of fuels (lower burning temperature).

Some industrial wastes, such as coal fly ashes [12,13], have been used for the production of belite-based clinkers, and the hydration characteristics of the resulting cements have also been studied [14,15]. However, belite-based clinkers require further consideration with regard to the phase transformation of C_2S, since the inert γ-C_2S is normally stable at room temperature. Some methods, e.g. chemical stabilization and rapid cooling technologies, have been used to preserve hydraulic high-temperature C_2S phases (α, α'_H, α'_L, and β) in clinkers [11,16–19]. In our previous study [20], electroplating sludge was successfully reused for the production

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of belite-rich cement (BRC) clinkers, and it was shown that the heavy metals, Ni, Zn, and Cr, can enable C_2S to be stabilized in the hydraulic β phase. This paper further describes the hydration characterization of the cement pastes resulting from BRC clinkers. Various inorganic wastes, including oyster shell ash, rice husk ash, water-treatment-plant (WTP) sludge, basic-oxygen-furnace (BOF) slag, and electroplating sludge, were employed as cement raw materials. The hydration of the cement pastes was studied by using the differential scanning calorimetry and thermogravimetric analysis (DSC–TGA) and ^{29}Si magic-angle spinning nuclear magnetic resonance (MAS/NMR) technology.

2. Experimental

2.1. Materials

The five inorganic wastes used as raw materials in this study were all collected in south Taiwan. After drying to constant weight in a 105 °C oven, the raw materials were crushed and ground into powders with a particle size of less than 75 μm (200 mesh). The chemical analysis for the raw materials was conducted with an inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer, Optima 2000 DV) following a microwave-assisted acid digestion procedure, in which the samples were digested with nitric, hydrochloric, and hydrofluoric acids at ~175 °C for 24 min in a high-performance microwave digestion unit (Milestone, MLS 1200 MEGA). The chemical compositions of the inorganic wastes are given in Table 1. Based on their major constituents, these inorganic wastes were selected to individually replace the traditional cement raw materials: oyster shell ash replaced limestone to provide calcium oxide; rice husk ash replaced sandstone to provide silica; WTP sludge replaced clay to provide both alumina and silica; BOF slag replaced iron ore and mainly provided iron oxide. The raw mixes for belite-rich clinkers were basically composed by weight of 63.9% oyster shell ash, 17.4% rice husk ash, 16.2% WTP sludge, and 2.5% BOF slag. The electroplating sludge, which contains nickel, zinc, chromium, and copper, was added to the raw mixes at 14% by weight, and the major composition involving CaO, SiO_2, Al_2O_3, and Fe_2O_3 was adjusted close to that of the basic raw mixes. To produce BRC clinkers, the raw mixes were pelletized into cylinders (approximately 35 mm in diameter and 8 mm in height) under a uniaxial pressure of 9.8 MPa, and then sintered in an electric furnace at 1250 °C for 3 h. Afterwards, the resulting clinkers were cooled to room temperature and ground into powder with a particle size of less than 75 μm. The BRC was thus prepared for the subsequent experiments.

2.2. Preparation of mortars

Since BRC has relatively low hydraulic reactivity, in order to satisfy the early strength requirements, commercial ordinary Portland cement (OPC) produced by Taiwan Cement Company was mixed with BRC at different weight fractions (shown in Table 2) to form blended cements, an approach which has been suggested in some previous studies [11,21]. The phase composition of OPC was 49.0% alite, 21.0% belite, 7.9% tricalcium aluminate, and 9.4% tetracalcium aluminoferrite, and its fineness was 345 m^2/kg (Blaine). The particle size distributions of OPC and BRC were measured by a laser diffraction particle size analyzer (Beckman Coulter, LS 230), and the results are given in Fig. 1. It was found that OPC and BRC had similar particle size distributions, and their average particle diameters were 17.12 μm and 20.85 μm, respectively. OPC and BRC were also analyzed by using an X-ray diffractometer (XRD, Bruker, D8 Advance) with Cu Kα radiation to acquire the mineralogical compositions, and the resulting patterns are presented in Fig. 2. Corundum was added into both the specimens as an internal standard to assist in the identification of crystalline phases. It is known that the most predominant crystalline phase in BRC is β-C_2S, while that in OPC is C_3S. Therefore, the blended cements, BC1, BC2, BC4, and BC8, would have different proportions of β-C_2S to C_3S, from low to high levels.

Blended cement mortars were prepared according to the standard method ASTM C109 [22]. The blended cements were mixed with graded standard sand and deionized water at a sand-to-cement ratio of 2.75 (w/w) and a water-to-cement ratio of 0.485 (w/w) by using an electric mixer, as specified in the standard practice ASTM C305 [23]. The cement pastes were immediately poured into 50-mm cubic molds to make specimens for determination of compressive strength, and moved to a moist closet where the humidity was about 95% and the temperature was kept at 23 ± 2 °C. After being in the moist closet for 24 h, the paste specimens were removed from the molds, and then immersed in water for further curing. The determination of compressive strength was

Table 2
The weight fractions of BRC and OPC in blended cements.

Blended cement	Weight fraction (%)	
	BRC	OPC
BC1	10	90
BC2	20	80
BC4	40	60
BC8	80	20

Table 1
The chemical compositions of the raw materials used for the production of BRC clinkers.

Chemical composition		Oyster shell ash	Rice husk ash	WTP sludge	BOF slag	Electroplating sludge
Metal content as oxides (wt.%)						
	CaO	74.8	1.0	0.6	36.9	4.3
	SiO_2	5.0	67.0	39.4	8.1	2.6
	Al_2O_3	1.2	1.1	16.1	1.2	0.2
	Fe_2O_3	0.4	0.4	4.6	29.1	10.1
	MgO	0.8	0.5	0.8	5.5	0.4
	Na_2O	1.2	0.2	0.7	ND[a]	0.8
	K_2O	0.2	3.2	2.4	ND[a]	0.1
Heavy metal (mg/kg)						
	Ni	ND[a]	ND[a]	ND[a]	ND[a]	125.336
	Zn	ND[a]	ND[a]	ND[a]	ND[a]	16.652
	Cu	ND[a]	ND[a]	ND[a]	ND[a]	43.787
	Cr	ND[a]	ND[a]	ND[a]	804	55.826
	Pb	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]
	Cd	ND[a]	ND[a]	ND[a]	ND[a]	ND[a]

[a] ND: not detected (<2 mg/kg).

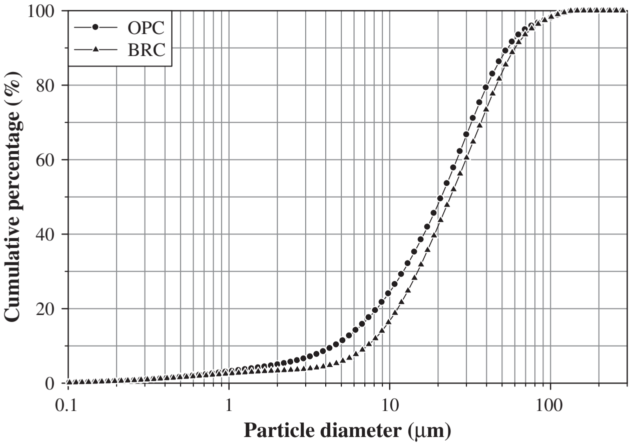

Fig. 1. Particle size distributions of OPC and BRC.

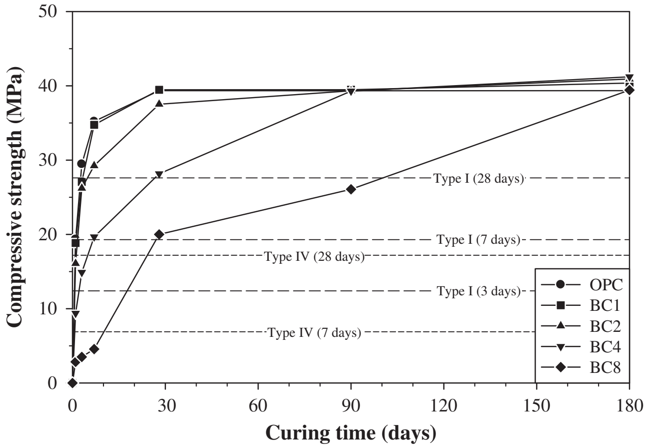

Fig. 3. The compressive strength development of the blended cement mortars.

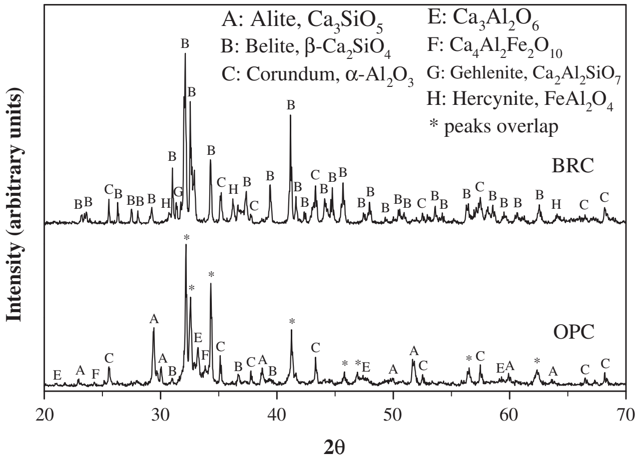

Fig. 2. XRD patterns of OPC and BRC.

performed at 1, 3, 7, 28, 90, and 180 days of age, and subsequently the hydration reactions of the cement pastes were interrupted by replacing water with acetone [24].

2.3. Analytical methodology

The simultaneous DSC–TGA (TA Instrument, SDT 2960) was used to study the hydration products in the blended cement pastes. Samples were first homogenized and ground into a fine powder, and then 40–50 mg was loaded into an alumina crucible for analysis. The furnace temperature was programmed to rise from ambient to 1000 °C at a heating rate of 10 °C/min. The analysis was performed under a dynamic nitrogen atmosphere (100 mL/min). In order to observe the chemical shift of linear polysilicate anions in calcium silicate hydrates (C–S–H), a solid-state MAS/NMR spectrometer (Bruker, Advance 400) was employed, and ^{29}Si spectra of the cement pastes at different ages were recorded at 79.49 MHz. The chemical shifts were converted to the value in ppm relative to tetramethylsilane (TMS) as a reference standard [25].

3. Results and discussion

3.1. Compressive strength development

Fig. 3 presents the compressive strength development of the OPC and blended cement mortars cured up to 180 days. It was found that the BC1 mortar was similar to the OPC mortar; in that the compressive strength increased rapidly within 7 days, and then slowed down considerably. The results in Fig. 3 also show that the early strength of the mortars (before 28 days of age) decreased with increasing BRC fraction in the blended cements. This can be explained by considering the diminution in C_3S. When the BRC fraction in the blended cement was 80%, the early strength of the resulting pastes developed slowly, and the later strength increased steadily between 28 and 180 days. The BC8 mortar had comparable compressive strength to the other blended cement mortars after curing for 180 days. These findings indicate that although the early strength of the blended cement mortars decreased due to partial deficiencies of C_3S, the β-C_2S from BRC hydrates in the later period, and thus provided sufficient compressive strength for the mortars. Fig. 3 also shows the requirements of compressive strength for Type I and IV Portland cements, based on the ASTM C150 [26] Standard Specification for Portland Cement. It was found that all the blended cements, except for BC8, satisfied the specification for Type I Portland cements, and in addition their 90-day compressive strength was comparable to that of commercial OPC products. Even though BC8 had good performance in later compressive strength, it still failed in both the strength requirements for Type I and IV Portland cements. From the above results, this study suggests that the BRC produced with the inorganic wastes has significant potential for engineering applications when appropriately blended with OPC, and that the BRC fraction below or equal to 40% should be acceptable for normal construction uses.

3.2. Thermal analysis for blended cement pastes

The hydration products in the blended cement pastes were examined by using the thermal analysis technique. Fig. 4 is a representative graph that shows the TG and DSC curves of the BC2 paste cured for 180 days. Several endothermic peaks accompanied by weight losses were observed during the heating procedure. Some researchers have studied the thermal behavior of hydration products in cement pastes [27–30], and the reactions occurring with elevated temperatures were described as follows: (1) The evaporable water is gradually eliminated from ambient to 100 °C. (2) The weight loss between 100 and 200 °C is mainly due to the decomposition of C–S–H. (3) The dehydroxylation of calcium hydroxide is observed at 440–550 °C. (4) The weight loss in a temperature range of 600–780 °C corresponds to decarbonation of calcium carbonate. Table 3 lists the weight losses related to the above compounds in the blended cement pastes. It can be seen that the amount of C–S–H in the pastes decreased with increasing the

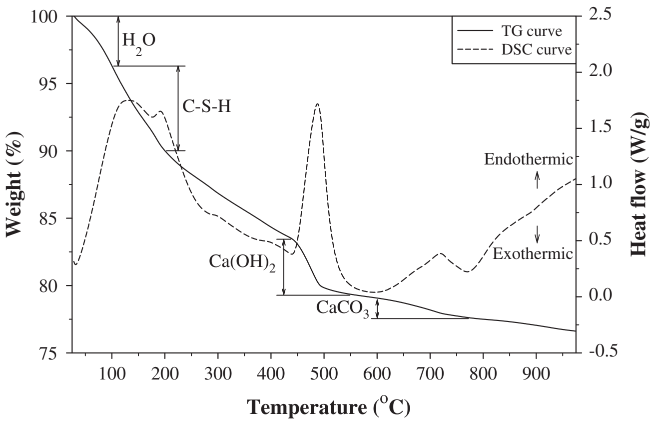

Fig. 4. TG and DSC curves of the BC2 paste cured for 180 days.

Table 3
The weight losses related to different compounds in blended cement pastes.

Blended cement	Curing time (days)	Weight loss (%)			
		H_2O	C–S–H	$Ca(OH)_2$	$CaCO_3$
BC1					
	1	2.07	3.47	2.53	3.17
	3	2.20	3.84	3.15	3.13
	7	1.93	4.27	3.79	3.13
	28	2.41	5.13	3.65	3.03
	90	3.80	6.20	4.42	3.03
	180	4.23	6.36	4.66	2.52
BC2					
	1	2.22	3.19	2.53	2.92
	3	2.25	3.72	2.91	2.95
	7	1.20	3.99	3.79	3.33
	28	3.03	5.30	3.94	2.78
	90	3.77	6.14	3.88	2.88
	180	3.72	6.23	4.26	2.44
BC4					
	1	1.99	2.85	1.73	2.77
	3	2.00	3.11	2.32	2.35
	7	1.16	3.50	2.53	2.80
	28	1.71	4.23	2.94	2.63
	90	3.42	5.85	3.28	3.28
	180	4.39	6.03	3.50	2.01
BC8					
	1	1.13	1.53	0.67	1.25
	3	1.26	1.69	0.60	1.45
	7	0.89	1.87	0.52	1.81
	28	1.74	2.19	0.87	1.52
	90	3.04	4.91	1.34	3.08
	180	3.81	5.73	1.58	2.38

BRC fraction, especially for days 1–28, but the difference at 90 or 180 days reduced significantly. In addition, the variation in the amount of calcium hydroxide, a product resulting from hydration of calcium silicates, was similar to that of C–S–H. It was also found that the amount of calcium hydroxide decreased with increasing BRC fraction, a finding which is compatible with the hypothesis about C_2S producing less calcium hydroxide than C_3S during hydration. These results imply that the β-C_2S from BRC hydrates in the later period, and thus increases the amounts of C–S–H and calcium hydroxide in the pastes. Furthermore, the increase of these hydration products can also support the results for the compressive strength development of the blended cement mortars.

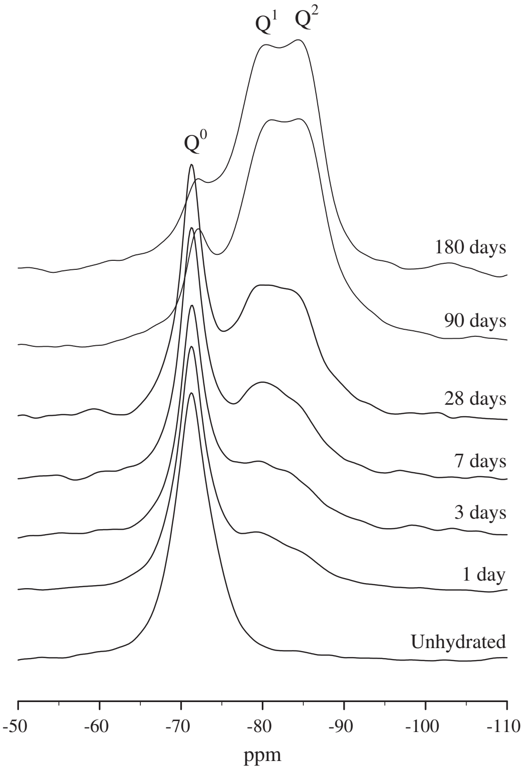

Fig. 5. ^{29}Si MAS/NMR spectra of BC1 and its pastes at different curing times.

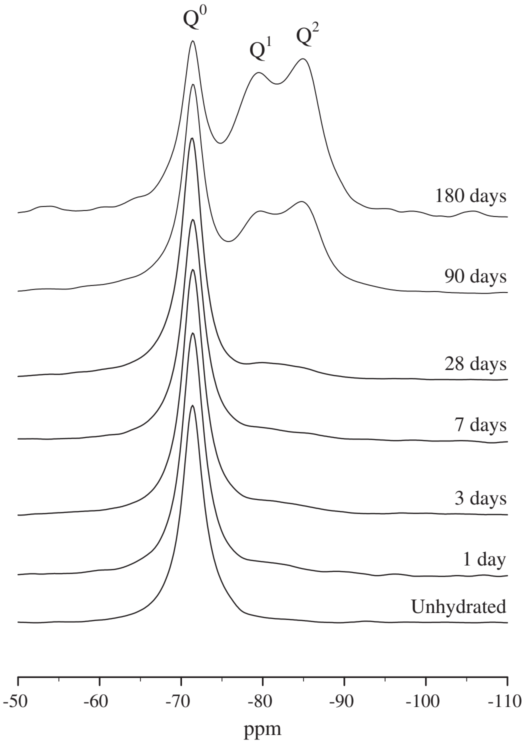

Fig. 6. ^{29}Si MAS/NMR spectra of BC8 and its pastes at different curing times.

3.2.1. ^{29}Si MAS/NMR analysis for blended cement pastes

The ^{29}Si MAS/NMR spectra of the BC1 and BC8 pastes cured up to 180 days are shown in Figs. 5 and 6, respectively. The ^{29}Si NMR technology has been used in cement and concrete research to study the hydration of calcium silicates by several researchers [31–33]. The chemical shifts can reflect different levels of condensation of silicate anions, i.e. the monosilicates (Q^0), the end groups of chains (Q^1), the middle groups in chains or cycles (Q^2), the chain branching sites (Q^3), and the three-dimensionally cross-linked groups (Q^4). It is known that the unhydrated calcium silicates contribute to the Q^0 (near −72 ppm) site, and the calcium silicate hydrates are generally dominated by the Q^1 (near −79 ppm) and Q^2 (near −85 ppm) sites. From Fig. 5, it is found that the signal intensity of Q^0 significantly decreased with the increase in curing time. On the other hand, the Q^1 and Q^2 signals initially appeared in the spectrum of the BC1 paste cured for 1 day, and their intensities increased with curing time. The BC1 paste cured for 180 days showed significant Q^1 and Q^2 signals and a relatively low intensity of Q^0. In the spectra of BC8 pastes (Fig. 6), the Q^1 and Q^2 signals are barely observed when the curing time was below 28 days, and the decrease in intensity of Q^0 was insignificant. However, after curing for 90 or 180 days, the BC8 pastes presented obvious signals of Q^1 and Q^2. These findings indicate that BC1 actively hydrates and C–S–H rapidly forms at early ages, whereas the hydration reaction of BC8 is inactive at the beginning, and a significant amount of C–S–H forms in the later period.

By considering the integral intensities corresponding to Q^0, Q^1, and Q^2, Justnes et al. [32] suggested equations (see Eqs. (1) and (2)) to determine the hydration degrees of the cement pastes (α) and to examine the average length of linear polysilicate anions (P_{Si}) in C–S–H, a method which has been used in some previous studies [34–36].

$$\alpha = \left[1 - \frac{I(Q^0)}{I^0(Q^0)}\right] \times 100\% \qquad (1)$$

$$P_{\mathrm{Si}} = \frac{2\left[I(Q^1) + I(Q^2)\right]}{I(Q^1)} \qquad (2)$$

In Eq. (1), $I(Q^0)$ and $I^0(Q^0)$ are the integral intensities of the Q^0 signal in a hydrated paste and an unhydrated cement, respectively. The calculated values of α and P_{Si} of the blended cement pastes are given in Table 4. It is seen that the hydration degree of the pastes increased with curing time, but decreased with increasing the BRC fraction in the blended cements at a specific curing time. The hydration degree of the BC1 paste was already 30% at 1 day of age, while that of the BC8 paste was only 8.5%. The BC1 pastes increased the hydration degree to 82.9% during the subsequent curing period. Meanwhile, the BC8 pastes hydrated slowly before 28 days of age, but had relatively high hydration degrees at 90 and 180 days. It is also noticed that although the BC4 paste cured for 90 days and the BC8 paste cured for 180 days had hydration degrees of only 70.5% and 65.2%, respectively, their compressive strength was comparable to that of the BC1 pastes. In terms of the average length of linear polysilicate anions in C–S–H, the P_{Si} values of the BC4 and BC8 pastes cured for 90 or 180 days were larger than those of the BC1 and BC2 pastes. Based on the results of the literature [37], it is found that the P_{Si} value is positively correlated with compressive strength of a mortar. The results from Table 4 show that the higher BRC fractions of the blended cements enhance the length of linear polysilicate anions in C–S–H at the later ages, and this may be an explanation for why the BC4 and BC8 pastes with relatively low hydration degrees can have similar compressive strength to the BC1 pastes.

Table 4
Hydration degrees (α) and average length of silicate anions (P_{Si}) in blended cement pastes.

Blended cement	Curing time (days)	α (%)	P_{Si}
BC1			
	1	30.0	3.25
	3	38.2	3.32
	7	42.6	3.47
	28	53.0	3.73
	90	80.4	4.03
	180	82.9	4.12
BC2			
	1	21.5	3.00
	3	27.9	3.14
	7	31.3	3.22
	28	53.6	3.45
	90	76.1	3.96
	180	81.0	4.04
BC4			
	1	19.0	2.87
	3	20.6	3.08
	7	27.3	3.13
	28	36.0	3.37
	90	70.5	4.16
	180	75.8	4.29
BC8			
	1	8.5	2.83
	3	8.7	2.98
	7	9.0	3.01
	28	10.2	3.21
	90	48.9	4.31
	180	65.2	4.77

4. Conclusions

Some conclusions from the present study can be drawn, as follows. The inorganic wastes are successfully used to totally replace cement raw materials for the production of BRC clinkers, which cannot only reduce the consumption of natural resources but also solve the problem of waste disposal. By appropriately blending with OPC, the compressive strength of the resulting mortars can meet the standard requirements, and is comparable to that of commercial OPC mortars in the later curing period. A BRC fraction in blended cements below or equal to 40% by weight is suggested for applications in normal construction uses. Since cement hydration is mainly dominated by calcium silicates, this study suggests that these blended cements, which can easily have different proportions of alite to belite, have high operational flexibility for various practical requirements. The present results also indicate that a higher BRC fraction in the blended cements makes the resulting pastes have longer linear silicate anions in C–S–H at the later ages. This could contribute to the similar later strength of the OPC and blended cement pastes. Future research could examine the other hydration characteristics of such blended cements, e.g. setting times, hydration heat, and sulfate resistance, or explore the stability of the heavy metals in these cement pastes.

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