



Preparation of belite cement from stockpiled high-carbon fly ash using granule-hydrothermal synthesis method



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HIGHLIGHTS

- Present a method for utilization of stockpiled high-carbon fly ash.
- Develop belite cement from fly ash with relatively higher strength.
- Propose granule-hydrothermal synthesis method of energy-saving.
- Characterize the compositional, microstructural and strength natures of the belite cement.

ARTICLE INFO

Article history:

Received 17 October 2015

Received in revised form 17 January 2016

Accepted 16 February 2016

Keywords:

Fly ash
Belite cement
Hydrothermal synthesis
Composition
Strength

ABSTRACT

Belite cement was prepared from lime and long-term stockpiled high-carbon fly ash by granule-hydrothermal synthesis at 97 °C followed by calcination at 800–1000 °C. The effects of the lime/fly ash ratio, dosage of Na₂O and calcination temperature on the phase compositions of the synthesized precursors and clinkers, and the properties of the cements were investigated. Belite cements with the flexural and compressive strengths at 28-day higher than 6.1 MPa and 32.8 MPa, respectively, were prepared. The results show that the quartz and mullite in the fly ash basically do not take part in the reactions. Adding 0.5–1.5% Na₂O promotes the hydrothermal reaction and formation of C–S–H and finally increases the formation of belite. α₁-C₂S and C₁₂A₇ are the main cementitious minerals in the clinker calcined at 800 °C, while β-C₂S and gehlenite present when the calcination temperature reached 900 °C or higher. Replacing ordinary portland cement partly for the belite cement might reduce the water requirement and increase the strengths.

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1. Introduction

Fly ash has been widely used as the mineral admixtures in cement production, concrete preparation, ready-prepared concrete products, and construction site reinforcement, etc. Low carbon-content, fine size and high reactivity are necessary for fly ash to be used in cement and concrete [1]. However, there are large quantities of high-carbon fly ashes discharged by wet process before the nineties of the last century [2]. These fly ashes are usually of coarse particle size and high carbon-content resulted from the relatively lower milling efficiency for coal powder and poorer burning technology in the last century. These fly ashes cannot to be used in cement and concrete for that it will severely affects the properties of cement and concrete, and only a small friction has gone to foundation construction. The majority of the fly ash has not been

effectively used and has been stockpiled for decades. The storage of fly ash not only occupies large areas of land, but also pollutes the environment. Disposal and utilization of the stockpiled high-carbon and low-quality fly ash is still an important subject to be investigated.

Mechanically and chemically technologies have been developed for improving the reactivity of fly ash [3]. However, these technologies are unable to reduce the carbon-content for fly ash, which adversely affects the properties of cement and concrete. Some researchers prepared belite cements by hydrothermally treating mixtures of fly ash and lime followed by calcining at temperatures lower than 1000 °C [4–22]. Among the researchers, Guerrero's group has done the most comprehensive works [10–22]. Mostly, slurries of fly ash and lime with high water/solid ratios (5:1–10:1) were prepared and autoclaved at about 180–200 °C for several hours under continuous stirring, and the precursors thus synthesized were dried and calcined at around 750–900 °C. The main hydraulic minerals of the clinkers so prepared are β-C₂S (or α₁-C₂S)

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and $C_{12}A_7$. This method is named here as slurry-autoclaving synthesis process. Slurry-autoclaving synthesis process gives a good condition for hydrothermal reaction between lime, fly ash and water, and results in higher contents of hydrated calcium silicates and hydrated calcium aluminate in the synthesized precursors, which leads to higher contents of the hydraulic minerals of the clinkers. However, in view of practice, the drying of slurries greatly increases the energy consumption, and autoclaving and stirring increase both the investment of the equipment and the complexity of the process. Nevertheless, the strength of the cement was lower. The compressive strengths of 1 cm × 1 cm × 1 cm mortar specimens were only 11–30 MPa [10], and the highest strength of 4 cm × 4 cm × 16 cm mortar specimen wet-cured at 40 °C for 28 days was only 15 MPa [17], as reported by Guerrero et al.

The present study used finely ground high-carbon fly ash as a raw material, and NaOH as an activator for accelerating the hydrothermal reaction, to increase the reaction rate of the reactant materials and the resulted hydration products in the precursors. Instead of slurry, the reactant mixtures were prepared as granular to simplify the drying process of the synthesized precursor and reduce the heat consumption. The method is thus known as granule-hydrothermal synthesis and low-temperature calcination method, or simply as granule-hydrothermal synthesis process. The effect of the original lime/fly ash ratio and the addition of alkali activators on the hydrothermal process, the mineral composition of the precursors and clinkers, and the mechanical strengths of the belite cements were investigated.

2. Experimental procedure

2.1. Materials

High-carbon fly ash from Xingtai Thermal Power Plant in Northern China wet-discharged in 80's last century and CaO (AR) were used as the raw materials. NaOH (AR) was used as the activator to accelerate the hydrothermal reaction. Gypsum and Chinese P-II 52.5 cement (OPC) from Jiangnan-Onoda Cement Corporation in Nanjing were used for preparing the cements. The fly ash was ground by an ultra-fine grinding mill to the residual over 45 μm sieve of 2.40%. The chemical composition, physical properties of the high-carbon fly ash, gypsum and P-II 52.5 cement are shown in Table 1.

2.2. Procedure

Raw batches with different CaO/fly ash mass ratios (CA/FA) and NaOH dosage shown in Table 2 were prepared. Though NaOH was actually used in the batches, it is referred as Na_2O hereafter for convenience, and the dosages are taken as the mass percentages of the total mass of CaO and fly ash.

Table 1
Chemical composition and physical properties of fly ash, gypsum and OPC.

Composition/property	Fly ash	Gypsum	OPC
<i>Chemical composition/wt%</i>			
SiO ₂	49.21	7.54	21.24
Fe ₂ O ₃	4.36	1.14	3.46
Al ₂ O ₃	29.46	2.64	4.83
CaO	2.26	27.4	64.0
MgO	0.80	0.55	1.37
TiO ₂	N/A	N/A	0.22
Na ₂ O	0.39	N/A	0.29
K ₂ O	0.28	N/A	0.66
SO ₃	0.18	39.59	2.40
Loss on ignition	10.08	0.50	1.59
Crystal water		17.63	
Density/gcm ⁻³	N/A	N/A	3.12
Blaine specific area/m ² kg ⁻¹	N/A	N/A	332
Residual, >45 μm/wt%	2.40	N/A	N/A
3-day compressive strength/MPa			37.2
3-day flexural strength/MPa			7.8
28-day compressive strength/MPa			60.9
28-day flexural strength/MPa			10.3

Table 2
Mix proportion of raw batch.

Batch No.	Mass proportion			CA/FA ratio	Na ₂ O [*] (wt%)
	CaO	Fly ash	NaOH		
A1	25	75	0	0.333	0
A2	25	75	0.674	0.333	0.5
A3	25	75	1.348	0.333	1.0
A4	25	75	2.022	0.333	1.5
B1	30	70	0	0.429	0
B2	30	70	0.674	0.429	0.5
B3	30	70	1.348	0.429	1.0
B4	30	70	2.022	0.429	1.5
C1	35	65	0	0.538	0
C2	35	65	0.674	0.538	0.5
C3	35	65	1.348	0.538	1.0
C4	35	65	2.022	0.538	1.5

* Added as equivalent NaOH and token as the percentage of the total mass of CaO and fly ash.

The raw batches were mixed with water by a cement paste mixer, with the water/solid ratios of 0.6–0.7 according to the CaO content of the batches, and placed in air-tight plastics bottles for 2 h to make the CaO slaked and without be carbonated. The raw batches were granulated to granules with the size of 8–12 mm by a small disc granulator, and steam-cured at 97 °C (a little below the boiling point) for 12 h. The steam-cured precursors, after being dried in a drying chamber at 80 °C for 6 h, were characterized by X-ray diffraction (XRD) with $CuK\alpha$ radiation, and thermal analysis (DSC/TG) in a dynamic nitrogen stream (flow rate = 100 cm³/min) at a heating rate of 10 °C/min.

The dried precursors were heated in a small muffle furnace at a ramp rate of 10 °C/min up to the designed temperatures and soaked for 60 min, and finally air-cooled to the room temperature. The minerals in the produced clinkers were analyzed by XRD, and the contents of free CaO were chemically analyzed by glycerol alcohol method [23].

Belite cements were prepared by grinding the clinkers with 7.0% gypsum to the residual over 0.08 mm sieve about 2.0%. Cement pastes with normal consistence were prepared and formed to 20 mm × 20 mm × 20 mm cubic specimens. Mortar specimens of 40 mm × 40 mm × 160 mm with the sand/cement (s/c) ratios of 3.0 and different water/cement (w/c) ratios adjusted according to the water requirements were prepared. The specimens were demolded after 24 h and cured for different ages in water of 20 °C. The strengths were tested at 3-day, 28-day and 90-day ages.

Scanning electron microscopy analysis (SEM) was performed, with an Ultra55 FE-SEM at the accelerating voltage of 15 kV, on the hydrothermally synthesized precursor, clinker and the hardened cement paste cured for 28 days. The precursor and paste samples were dried at 60 °C for 6 h before the analysis.

3. Results and discussion

3.1. Influence of CA/FA ratio and Na₂O dosage on hydrothermal synthesis

3.1.1. XRD analysis

Fig. 1 shows the XRD patterns of the hydrothermally synthesized precursors from the raw batches with different original CA/FA ratios, added with 1.0% Na₂O. The main crystalline components are quartz and mullite, portlandite (Ca(OH)₂), tricalcium aluminate hydrate (3CaO·Al₂O₃·6H₂O, C₃AH₆), and C–S–H gel with very poor crystallinity. The quartz and mullite are the original minerals from fly ash, indicating that these two minerals nearly do not take part in the hydrothermal reaction below 100 °C. There is also a little amount of calcite (CaCO₃) present probably resulted from the carbonation during the drying of the samples. Just as that was expected, the greater the CA/FA ratio was, the stronger the peaks associated to Ca(OH)₂ appear. The broad hump between 28° and 30°, which consists of four overlapped peaks associated to Ca(OH)₂, mullite, C–S–H and calcite, respectively, becomes broader and stronger as the CA/FA ratio was increased from 0.333 to 0.466. Since C–S–H is with very poor crystallinity and usually leads to broad diffraction peaks, the broadening and strengthening of the hump indicates the increase of C–S–H formed. Though very weak,

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