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Preparation and properties of self-pulverizing calcium sulfoaluminate cement

Xiong Zhang, Ming Zhao *, Yongjuan Zhang

Key Laboratory of Advanced Civil Engineering Materials of the Ministry of Education, Tongji University, Shanghai 201804, China

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ABSTRACT

The transition of β-C_2S to γ-C_2S can be used to pulverize cement clinkers for saving grinding energy because the volume expansion occurs in this process. Self-pulverizing calcium sulfoaluminate cement (SPCSA) was prepared and optimized through controlling the polymorphic transition. The influences of preparing technologies and compositions on pulverization were investigated. Quantitative XRD was conducted to define phase compositions of clinkers, and sieve analysis was used to evaluate the pulverization degree. Mechanical properties and grinding energy consumption of SPCSA were tested and compared with ordinary calcium sulfoaluminate cement (CSA). The results show that the pulverization degree and properties of SPCSA are influenced by sintering temperature, cooling rate, chemical impurities and mineral compositions. The appropriate sintering temperature is 1280–1350 °C, and the cooling rate should not exceed 500 °C/min. Meanwhile, the optimal mineral compositions of SPCSA are proposed. The grinding test reveals that SPCSA can save grinding energy by 60–75% in comparison with stabilized CSA.

1. Introduction

Cement industry requires a large amount of raw materials and energy, and emits 5–7% of global anthropogenic CO_2 [1–4]. Nowadays, low energy consumption and CO_2 emissions become a research trend. It could be summarized as follows: (a) the development of new manufacturing technologies; (b) the use of alternative fuels (tires, sewage sludge, etc.) in cement kilns; (c) the substitution of clinker by industrial by-products like fly ash and ground granulated blast furnace slag; (d) the addition of grinding aids with a view to improving grinding efficiency; and (e) the development of new types of binders with intrinsically lower energy requirements and CO_2 emissions during manufacture [1–11].

Calcium sulfoaluminate cement (CSA) has been developed by the China Building Materials Academy in the 1970s [12,13]. In 2009, more than 1.2 million tons of CSA was produced in China [14]. Because of high early strength and low alkalinity, it has been developed quickly and applied in a wide range, e.g., high early strength concrete, self-leveling topping mortar, and high performance glass-fiber-reinforced composites [13]. CSA mainly consists of yeelimite ($C_4A_3\$$), belite (C_2S) and ferrite (C_4AF) [7,13]. In production, its sintering temperature is in the range of 1200–1350 °C, rather than 1400–1500 °C of OPC [12,15]. Lime requirement and CO_2 emissions are also markedly reduced due to the low Ca content in CSA [12,16,17]. Consequently, CSA production is characterized by lower sintering energy, less lime requirement and lower CO_2 emissions. In addition, CSA clinker is easier to grind than OPC [15].

In cement manufacturing, 30–40% of electricity consumption is used for the final cement clinker grinding [1,3,4]. It is noteworthy that grinding is a low-efficiency process. Less than 5% of the energy is used for the increase of cement surface area, while more than 95% of the energy turns into heat without avail [1]. Grinding aids can improve grinding efficiency, but it is limited to the range of 10–30% [1,8]. It is a challenge to make great improvements in grinding efficiency. However, it is a novel method to pulverize cement clinker using its inner stress caused by the polymorphic transition of β-C_2S to γ-C_2S, which could save considerable energy in the grinding process.

C_2S makes up 20–30 wt.% of CSA clinker and normally presents as the β-phase. There are five polymorphs (α, α'_L, α'_H, β, γ), that are stable in different temperature ranges [18,19]. Commonly, neither α-C_2S nor α′-C_2S exists in final cement clinkers because they are readily to transform to β-C_2S on cooling to room temperature [18]. But β-C_2S and γ-C_2S coexist because the reversible polymorphic transition of β–γ takes place below 500 °C [18]. The transition of β to γ could be enhanced by (a) prolonged holding time at high temperatures, (b) low cooling rates, and (c) the absence of foreign ions such as sodium and potassium that could stabilize the β-form [16,18,19]. Densities of β-C_2S (monoclinic) and γ-C_2S (orthorhombic) are 3.28 g/cm^3 and 2.97 g/cm^3, respectively. The β to γ transformation leads to

* Corresponding author. Address: School of Materials Science and Engineering, Tongji University, Cao'an Road 4800, Shanghai 201804, China. Tel.: +86 13817896971; fax: +86 21 65752186.
E-mail address: zhaoming_1002@163.com (M. Zhao).

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Table 1
Oxide compositions of industrial raw materials (by mass %).

Oxide	Limestone	Bauxite	Gypsum	Quartz sand
SiO_2	0.44	7.15	0.50	97.00
Al_2O_3	1.42	71.70	0.72	–
CaO	54.30	0.67	31.45	–
Fe_2O_3	0.08	3.83	0.05	–
MgO	0.71	0.90	1.21	–
K_2O	0.04	0.45	0.37	–
Na_2O	0.07	0.12	0.05	–
TiO_2	–	1.66	–	–
SO_3	–	–	44.92	–
Loss	42.52	13.87	20.72	3.00

volume expansion and the expansion stress is high enough to pulverize the clinker nodules [19]. It could be used to save grinding energy of the final cement. But γ-C_2S is considered as inert and has poor hydraulic properties. Its content must be controlled to an appropriate range, in which the balance between energy saving and hydraulicity could be obtained.

This paper deals with the possibility of preparing self-pulverizing calcium sulfoaluminate cement (SPCSA) through controlling the transition of β-C_2S to γ-C_2S. The influences of preparing parameters (sintering temperature, and cooling rate) and compositions of raw mixtures on the polymorphic transition and pulverization were investigated. Its physical and mechanical properties were tested and compared with stabilized CSA. Finally, the energy saving was evaluated through grinding energy consumption test.

2. Experimental procedure

2.1. Raw materials and samples preparation

2.1.1. Raw materials

Chemical reagents (Al_2O_3, Fe_2O_3, $CaCO_3$, $CaSO_4$ and SiO_2) and industrial raw materials (Table 1) were used to prepare cement clinkers. Target phase compositions and batch formulations are given in Table 2. C-1–C-10 were synthesized from chemical reagents, and C-11–C-12 were prepared from industrial raw materials. In addition, analytical reagents (Na_2O, P_2O_5, B_2O_3, Cr_2O_3 and K_2O) were used as chemical impurities or stabilizers on β-C_2S to study influences of chemical compositions on the β to γ transformation.

2.1.2. Preparation of clinker

Raw materials were dried in an oven at 105 °C for 4 h and ground to pass 80 μm mesh sieve. After thorough homogenization with appropriate amount of water, raw mixtures were pressed into saggers and then introduced into the laboratory furnace (muffle furnace). The batch compositions were subjected to sintering temperature between 1100 °C and 1500 °C. The sintering duration at the maximum temperature was 1 h. Subsequently, they were cooled down to room temperature at designed cooling rates.

The following rates of cooling were selected: (a) slow (cooled in the furnace at a cooling rate of 2 °C/min), (b) moderate (cooled in the natural air at a cooling rate of 60 °C/min), (c) accelerated (cooled by an electric fan at a cooling rate of 500 °C/min) and (d) fast (cooled by water spray at a cooling rate of 1200 °C/min and then washed with acetone).

2.1.3. Preparation of cement

The cement was obtained by grinding SPCSA clinker with a suitable amount of dihydrate gypsum (C$$H_2$), which was determined by Eq. (1). Assuming the amount of clinker is 100, dihydrate gypsum (G) is

$$G = 0.13M\frac{[C_4A_3S]}{[SO_3]} \quad (1)$$

where [$C_4A_3$$] is the mass fraction of $C_4A_3$$ in the clinker, [SO_3] is the mass fraction of SO_3 in dihydrate gypsum, and M is the molar ratio of C$$H_2$ and $C_4A_3$$. M was 0.8 in this paper. The specific surface area of the final cement was controlled in the range of 320–350 m^2/kg.

2.2. Test methods

2.2.1. Quantitative X-ray diffraction

Mineral compositions of the prepared clinkers were characterized through quantitative X-ray diffraction (QXRD). It was conducted in a Rigaku Geierflex diffractometer with a Cu Kα radiation source in 10–80° 2θ range, scan rate of 0.02° 2θ, 4 s per step. The quantitative phase analysis was performed using GSAS EXPGUI software following a Reference Intensity Ratio (RIR) and the Rietveld refinement techniques. Polymorphic transition ratio (R_t) was calculated by the following equation

$$R_t = \frac{M_\gamma - C_2S}{M_\beta - C_2S + M_\gamma - C_2S} \times 100\% \quad (2)$$

where $M_{\gamma-C_2S}$ and $M_{\beta-C_2S}$ are weight percentages of γ-C_2S and β-C_2S in the sample.

In addition, glycerin–alcohol method was performed to determine the free lime (f-CaO) contents in the prepared samples.

2.2.2. Sieve analysis and evaluation of pulverization

The particle size distribution of pulverized clinker was determined by a sieve analysis. A representative sample of the pulverized clinker was passed through a stack of sieves arranged in order of decreasing size of the openings of the sieve. After 15 min of screening on automatic sorting machine, the residues on different screens were weighed. Finally, particle size distribution was calculated and analyzed. Pulverization ratio (R_p) was designated as the weight percentage of the fine particles passing 1.02 mm (0.040 in.) mesh sieves. It was used to evaluate the pulverization degree.

2.2.3. Tests of physical and mechanical properties

The SPCSA samples were tested for their specific gravity (ρ), specific surface area (S), water requirement of normal consistency (W), setting time and compressive strength according to Chinese Standards (GB/T 208, GB/T 8074, GB/T 1346, GB/T 17671).

2.2.4. Grinding energy consumption

The grinding test was performed in a laboratory mill (Φ330 mm × 580 mm, 28 kW) with 1 kg of medium steel rods (Φ20 mm × 20 mm) and 0.25 kg of small steel rods (Φ10 mm × 20 mm) as grinding media. The grinding material was

Table 2
Design of mineral compositions (wt.%) and batch formulations (expressed as oxides, wt.%).

Compositions	Samples											
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12
Target phase compositions												
C_2S	30	25	30	25	25	25	15	20	35	50	38.5	49.4
$C_4A_3$$	60	65	65	55	45	35	65	65	65	40	53.2	45.6
C_4AF	10	10	5	20	30	40	20	15	0	10	4.5	4.7
Batch formulations												
SiO_2	10.6	8.7	10.5	8.7	8.7	8.7	5.3	7.0	12.2	17.4	9.5	12.3
Al_2O_3	32.2	34.6	33.6	31.7	28.8	25.9	36.8	35.7	32.5	22.1	21.7	16.2
CaO	46.2	47.8	45.7	45.7	46.7	47.6	42.8	43.9	46.8	51.9	33.7	34.9
Fe_2O_3	3.3	3.3	1.7	6.6	9.9	13.2	6.6	4.9	0	3.3	1.0	1.1
SO_3	7.9	8.5	8.5	7.2	5.9	4.6	8.5	8.5	8.5	5.2	4.9	4.2
MgO	–	–	–	–	–	–	–	–	–	–	0.9	0.7
K_2O	–	–	–	–	–	–	–	–	–	–	0.2	0.1
Na_2O	–	–	–	–	–	–	–	–	–	–	0.02	0.07
TiO_2	–	–	–	–	–	–	–	–	–	–	0.4	0.4
Loss	–	–	–	–	–	–	–	–	–	–	29.5	29.8