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Preparation of high-performance cementitious materials from industrial solid waste

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HIGHLIGHTS

- Sulfoaluminate cementitious materials were produced by using 100% industrial solid wastes.
- Influence of raw mix composition and calcination temperature on the properties of Sulfoaluminate clinker was discussed.
- Sulfoaluminate cementitious materials were produced in a 1 t/d industrial rotary kiln.

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ABSTRACT

Sulfoaluminate cement exhibits a good dimensional stability, an early strength, a high strength, a high resistance to chemical attack (from seawater, sulfates and chlorides), a low energy consumption and low carbon-dioxide emissions during production. However, sulfoaluminate cement factories traditionally use limestone, bauxite and gypsum as materials, which places significant pressure on these natural resources. This study aimed to investigate the feasibility of substituting traditional raw materials with industrial solid wastes in sulfoaluminate clinker production. It was achieved by sintering a mixture of industrial solid wastes (coal gangue: 8%–15%, flue gas desulfurization gypsum: 25%–35%, aluminum slag: 30%–35%, carbide slag: 30%–35%) at 1150–1300 °C. The mineralogical composition of the clinker was $C_4A_3\overline{S}$, C_2S and C_4AF. The compressive strength of hydrated specimens reached as high as 75 MPa after a 28 d curing. This research provides a feasible and promising way to produce high-value products using industrial solid wastes and may promote their large-scale utilization.

1. Introduction

China is the largest cement-producing and -consuming country. Cement production in China reached 2.42 billion tonnes in 2013 [1], which accounted for 58.6% of global production [2]. Ninety-five percent of the cement was ordinary Portland cement (OPC). The OPC industry requires a large amount of natural resources and energy, and emits 5%–7% of global greenhouse gases [3–6]. Low-carbon, energy-saving and environment-friendly cement varieties are highly expected as alternative products for OPC. Increased attention has been given to the development of sulfoaluminate cement (SAC) because of its lower energy consumption and CO_2 emission during production [7,8]. SAC clinker consists mainly of calcium sulfoaluminate ($C_4A_3\overline{S}$, yelimite), dicalcium silicate (C_2S) and ferrous phases (C_4AF, C_6A_2F or C_6AF_2). SAC clinker can be calcined at 1200–1300 °C, which is 100–150 °C lower than in OPC clinker production [9]. It has a 1/3 lower CaO content compared with OPC clinker, meaning up to 40% less CO_2 emission [10–12]. SAC has characteristics of high mechanical strength, especially high early-age strength, rapid setting, low permeability, and low alkalinity, etc. It does have the potential to replace PC in a wider range.

The main obstacle to the application of SAC on a massive scale is its high cost of materials, which requires expensive natural bauxite of ~50–80 US$/t. If the SAC materials can be provided by the widespread solid waste, its production cost may be greatly lowered and its enormous potential will be sufficiently released. According to data from China National Bureau of Statistics, total industrial solid waste, including tailings, fly ash, coal gangue, smelting waste slag, furnace clinker, and so on, reached 32.789 billion tonnes in 2013 in China [13]. These industrial solid wastes may pollute soil, groundwater, air and impact human health [14]. Bridging the gap between solid waste and SAC can benefit both environment protection industry and building materials industry.

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Some industrial wastes, such as tailings, coal gangue, smelting waste slag, fly ash, acidic waste rock and phosphogypsum, have already been used as materials to produce cement clinker or concrete [15–17]. Pace used alumina powder from secondary aluminum manufacture, and anodization mud from the production of anodized aluminum to partially or totally replace bauxite in the production of SAC [18]. Singh demonstrated that it is possible to prepare calcium sulphoaluminate–aluminoferrite-based special cements with strength values that are comparable to OPC using phosphochalks from a fertilizer plant [19]. Rungchet investigated the use of industrial waste materials compared with fly ash, aluminum-rich sludge and flue gas desulfurization gypsum in the production of calcium sulfoaluminate-belite cement using a hydrothermal-calcination method [20]. Literature [15–20] also involve SAC preparation by jointly using industrial waste materials, such as tailings waste, fly ash, and natural minerals. However, very few reports are given about entirely using waste as raw materials.

This work investigated the possibility of using 100% waste as a raw material in SAC clinker production. This work shows the feasibility of producing sulfoaluminate clinker from a mixture of coal gangue, flue-gas desulfurization (FGD) gypsum, aluminum slag and carbide slag as raw materials. This solid waste combination is easily accessed in some typical industrial gardens of China. The SAC clinker quality was investigated to evaluate the clinker chemical compositions by X-ray fluorescence (XRF), and X-ray diffraction (XRD) was used to determine the phases in the clinker. An electronic universal-testing machine was used to test its strength. Clinker setting times were determined from the VICAT measurements. The effects of different process parameters such as raw mix composition, sintering temperature on the phase formation and strength were also investigated. Excellent clinker performances and good application potential of the technology were proved.

2. Experimental program

2.1. Raw materials

Chemical reagents (Al_2O_3,$CaCO_3$,$CaSO_4{\cdot}2H_2O$) and industrial raw materials (coal gangue, aluminum slag, FGD gypsum, carbide slag) were used to prepare clinkers. Chemical reagents were used as a reference material to manufacture a pure calcium sulfoaluminate phase under the same constraints. The reagent-grade chemicals used for the synthesis of SAC clinkers were calcium carbonate (99% $CaCO_3$; Aladdin), aluminum oxide (100% Al_2O_3; Aladdin), and calcium sulfate dihydrate (99% $CaSO_4{\cdot}2H_2O$; Aladdin). FGD gypsum was collected from Liaocheng coal-fired power plants, aluminum slag was supplied by the Chiping XINFA Group, Shandong, carbide slag was from Liaocheng acetylene company, and the waste coal-gangue was from Taifeng Group Ming area in Taian, Shandong.

The main oxide compositions of the initial raw materials were analyzed chemically by wavelength-dispersive XRF. The chemical composition of the raw materials is presented in Table 1.

2.2. Experimental devices

The devices that were used to manufacture sulfoaluminate clinker is shown in Table 2.

2.3. Mix design

Cement clinker was manufactured in the laboratory. Preliminary series experiments on material proportion were conducted before the research. The detailed experimental program consisted of the following steps:

(1) All materials were dried in an oven at 160 °C to constant weight, ground and sieved through a 200-mesh sieve.
(2) Raw mix preparation.

The cement modulus that was used in the investigation was defined as follows (Eq. (1)–(3)). Typically, according to previous studies [21], the cement clinker modulus is controlled at an alkalinity modulus C_m (0.90–1.1), an alumina–sulfur ratio P (~1.9) and an alumina–silica ratio N (~3.4). Table 3 provides the raw mix compositions along with their C_m, P and N values.

$$\text{Alkalinity modulus } (C_m): C_m = \frac{CaO - 0.7TiO_2}{1.87SiO_2 + 0.73(Al_2O_3 - 0.64Fe_2O_3) + 1.40Fe_2O_3} \quad (1)$$

$$\text{Alumina-sulfur ratio } (P): P = \frac{Al_2O_3 - 0.64Fe_2O_3}{SO_3} \quad (2)$$

$$\text{Alumina-silica ratio } (N): N = \frac{Al_2O_3}{SiO_2} \quad (3)$$

(3) Raw materials in predetermined proportions were mixed thoroughly. After thorough homogenization, the raw mixture was pressed and molded into cylindrical samples of 30-mm diameter and 5-mm height.
(4) The raw material cubes were dried in a hot-air oven at 160 °C for 6 h and then fired in an electric-resistance holding furnace at firing temperatures from 20 °C to 1280 °C. The clinker underwent annealing at 1280 °C for 1 h followed by fast cooling in air to produce the clinker.
Six sets of compositions were fired at 1280 °C for 1 h to investigate the effects of industry waste and C_m on the formation of phases in the SAC clinkers. C3# was fired at different temperatures (1000 °C, 1050 °C, 1100 °C, 1150 °C, 1200 °C, 1250 °C, 1300 °C) at 10 °C/min for 1 h to investigate the effects of firing temperature on SAC clinker phase formation.
(5) Grinding
A grinding test was performed in a laboratory mill (Φ 330 mm × 580 mm, 1.1 kW) with 1 kg of medium steel rods (Φ 20 mm × 20 mm) and 0.25 kg of small steel rods (Φ 10 mm × 20 mm) as grinding media. Clinker powder was passed through a 200-mesh sieve.

Table 1
Main composition of raw materials (wt%).

	Al_2O_3	SiO_2	Fe_2O_3	CaO	SO_3	MgO	TiO_2	BaO	R_2O[a]	LOI[b]
Carbide slag	1.94	2.59	0.29	69.89	–	–	0.03	–	–	25.23
Aluminum slag	72.66	3.78	0.70	1.73	1.63	6.17	0.29	0.07	4.36	4.33
Coal gangue	21.82	52.14	4.49	0.93	1.32	4.67	0.41	0.01	3.53	10.25
FGD	–	6.84	0.63	37.87	46.96	–	0.14	0.04	0.87	6.57

[a] alkaline oxide (K_2O, Na_2O).
[b] Loss on ignition at 950 °C.