



Synthesis of belite sulfoaluminate-ternesite cements with phosphogypsum



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ABSTRACT

Phosphogypsum (PG) is an industrial byproduct from phosphoric acid production. In order to facilitate the use of PG, belite sulfoaluminate-ternesite cements were produced with high amounts of PG. This work regards the laboratory production of belite sulfoaluminate-ternesite cements by using a new synthesis method. Using a secondary heat treatment step, the method achieves the coexistence of ye'elimite and ternesite. Quantitative X-ray powder diffraction and electron microscopy were used to analyze the phase composition of clinkers. The secondary heat treatment between 1100 and 1200 °C can significantly facilitate the formation of ternesite in the clinkers. The presence of large amount of ternesite results in a decrease in early strength, but the hydration of ternesite at later ages can increase the strength after 56 days of hardening. The hydration products of pure ternesite and the clinker containing ternesite were also investigated. The results show that pure ternesite can hydrate at a slow rate, and the addition of ye'elimite promotes the hydration of ternesite and the formation of ettringite. The ettringite formation for the clinker containing ternesite mainly depends on the dissolution of gypsum originating from the hydration of ternesite.

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1. Introduction

Phosphogypsum (PG) is a solid waste from the production of phosphoric acid by the wet process. It is composed primarily of calcium sulfate dihydrate and partially of some impurities, such as phosphate, fluorides, sulfate ions and organic matters [1,2]. At present, the output of PG is estimated to be around 280 million tons per year all over the world and more than 55 million tons per year throughout China [3,4]. PG management is one of the most serious problems faced by the phosphate industry. In China, only 10% PG production is recycled as building materials, agricultural fertilizers or soil stabilization amendments and as setting controller in the manufacture of Portland cement [1]. The rest is disposed of without any treatment. Such a huge amount of PG not only occupies large land areas but also causes severe pollution to the surrounding environment due to some of its harmful impurities. Consequently, it is urgent to utilize PG effectively.

Calcium sulfoaluminate (CSA) cement generally refers to cements that are based on clinkers containing ye'elimite, belite and

ferrite in various proportions as their major phases. The burning temperature for the production of CSA clinkers is about 1250–1350 °C, and the final cements are manufactured by adding calcium sulfate to CSA clinkers. Due to lower energy used and CO₂ emitted during production, CSA cement is promoted as a promising alternative to ordinary Portland cement [5]. CSA cement can exhibit rapid setting, high early-age strength and slight expansion because of the fast reaction of ye'elimite with calcium sulfates. Over the past few years, many types of calcium sulfoaluminate-based cements have been developed for a wide range of applications [6]. Currently, a class of belite sulfoaluminate (BSA) cements is receiving a great deal of attention [7,8]. The cements can be classified as belite-rich materials, containing higher proportion of belite and lower proportion of ye'elimite than classical CSA cements. This means that BSA cement production demands less aluminum and allows alumina-containing industrial byproducts to be used to replace bauxite. Moreover, the sulfate requirement for BSA cement production allows sulfate-containing industrial wastes to be used as raw materials [9]. In this work, PG was incorporated into the production of BSA cements to utilize PG effectively.

Usually BSA clinkers can be produced by firing a mixture of limestone, clay, bauxite, natural gypsum (NG) and iron ores to

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provide the necessary CaO, SiO₂, Al₂O₃, SO₃ and Fe₂O₃ required for phase formation. However, a small amount of gypsum inevitably decomposes at temperatures above 1200 °C, which can result in a shortage of gypsum and affect the formation of ye'elimite [10]. In order to minimize sulfur emissions during the firing process, the raw materials can be burned in covered and sealed crucibles in the laboratory furnace [10]. Furthermore, an excess of gypsum should be added to raw materials to promote the formation of ye'elimite [11,12]. In this study, considering the formation of ye'elimite and the utilization of PG, the amount of PG added to raw mix increased accordingly. The excessive PG can make anhydrite phase remain in the produced clinkers.

BSA cements may contain minor phases such as ternesite (C5S2 \bar{S}) which is also called calcium sulfoasilicate when excess gypsum is incorporated into raw materials. Previous investigations on systems containing CaO, SiO₂, Al₂O₃ and CaSO₄ indicated that at about 1200 °C, ternesite formed as an intermediate phase instead of belite and anhydrite, in addition to ye'elimite [13,14]. Wang et al. studied high-temperature reactions of the systems during the burning process [15]. The results showed that at 1150–1250 °C, belite reacted with anhydrite to form ternesite, which decomposed to the above two components at temperatures higher than 1250 °C. The formation of ternesite is linked to the clinkering process and the proportioning of raw materials [12]. Several studies reported that ternesite is only slightly reactive at later ages of hydration or even inert [16–19]. Sherman et al. studied the hydraulic properties of pure ternesite for up to 2 years [20]. The results indicated that the hydration of ternesite is very slow, but more extensive with longer curing ages. They also found that although ternesite hydrates very slowly, it can contribute to the mechanical strength of cements, particularly at later ages [14]. According to the literature [21], ternesite is a reactive phase when part of belite calcium sulfoaluminate ferrite clinker and it is more reactive than belite.

The purpose of this work is to investigate the utilization of PG as raw materials for the production of belite sulfoaluminate-ternesite cements. The formation of ternesite in belite sulfoaluminate cements can significantly facilitate the use of PG. The production of belite sulfoaluminate-ternesite cement is not straightforward because of the discrepancy in optimum firing conditions for ye'elimite and ternesite. Ye'elimite forms rapidly at about 1250 °C in conventional calcium sulfoaluminate clinker production while ternesite mostly decomposes above 1200 °C [21]. Therefore, this paper reports a new protocol for the production of belite sulfoaluminate-ternesite clinker based on two successive firing steps. The influence of temperature history on the formation of ternesite and the final properties of the resulting cements were studied. Additionally, the hydration behavior of the produced belite sulfoaluminate cements and synthetic ternesite were also discussed to evaluate the reactivity of ternesite.

2. Experimental

2.1. Raw materials

The raw materials used for the synthesis of belite sulfoaluminate-ternesite clinkers were limestone, bauxite and PG. The sample of PG was obtained from a phosphate fertilizer plant in Yun Nan, China. PG from different sources may differ with respect to the constituents and their amounts. Limestone and bauxite were gained from the market in Chongqing, China. The chemical compositions of the raw materials are shown in Table 1. The mineralogical phase compositions of the raw materials were also analyzed and the result is presented in Table 2. All the materials were dried in an oven to constant weight, and then ground to pass through a 80 μ m sieve.

Table 1
Chemical composition of raw materials used for cement clinkers (wt.%).

Oxide	Limestone	Bauxite	PG
CaO	44.79	0.20	31.04
SiO ₂	8.75	19.78	9.10
Al ₂ O ₃	2.71	51.73	0.46
Fe ₂ O ₃	1.59	8.94	0.17
MgO	1.26	0.30	0.03
P ₂ O ₅	0.05	0.10	0.69
SO ₃	0.26	0.16	39.02
LOI	38.60	12.38	18.50

Table 2
Mineralogical composition of raw materials used for cement clinkers (wt.%).

Limestone	Bauxite	PG
Calcite 91.2	Diaspore 58.3	Gypsum 92.5
Quartz 8.8	Kaolinite 18.2	Quartz 7.5
	Hematite 8.6	
	Quartz 14.9	

The reagent-grade chemicals used for the synthesis of pure ternesite were calcium carbonate and calcium sulfate dihydrate. Silica fume was used as silica provider, and the chemical composition is listed in Table 3. It shows that silica fume consists primarily of silica dioxide. The surface area of silica fume was 20,000 m²/Kg. The high silica content and large surface area of silica fume can promote the formation of belite at low temperatures, and thus facilitate the synthesis of pure ternesite.

2.2. Synthesis of pure ternesite and belite sulfoaluminate-ternesite clinkers

Pure ternesite was synthesized from a stoichiometric mixture of calcium carbonate, calcium sulfate dihydrate and silica fume. These materials were homogenized and then pelletized to the size of approximately 20-mm diameter with 10% of water. Afterwards, the pellets were subjected to different firing temperatures between 1100 °C and 1250 °C. The time duration at the temperature peak was varied between 2 and 15 h. The sample so prepared was followed by cooling at room temperature and finally were ground to pass through a 80 μ m sieve.

In this work, the composition of two different clinkers has been studied. Belite sulfoaluminate-ternesite clinker that underwent secondary heat treatment (Clinker B) was compared to belite sulfoaluminate clinker prepared without secondary heat treatment (Clinker A). For the synthesis of the two clinkers, the mix proportion of limestone, bauxite and PG are 60.6%, 15.7% and 23.7%, respectively. The mixture of raw materials was ground and pre-homogenized in a ball mill, then the powder was pressed into a disk mold (ϕ 50 mm \times 8 mm). The disks were fired according to the protocols shown in Fig. 1. A first cycle consisted of firing at 1270 °C for 30 min and a subsequent air-quench to prepare Clinker A. A second firing cycle at 1100–1200 °C for 1 h followed by air-quenching was carried out to produce Clinker B. The clinkers so prepared were ground in a ball mill to reach the target Blaine surface area of 350 m²/kg.

Table 3
Chemical composition of silica fume (wt.%).

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	LOI
1.20	89.25	6.43	0.75	0.54	1.45

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