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Mechanical properties and hydration mechanisms of high-strength fluorogypsum-blast furnace slag-based hydraulic cementitious binder

Huang Xuquan *, Jiang Mingming, Zhao Xiaorong, Tang Cilai

College of Hydraulic & Environmental Engineering, China Three Gorges University, Yichang 443002, China

HIGHLIGHTS

- FBB was composed of 40–50% fluorogypsum, 5% Portland cement, 45–55% blast furnace slag and 1% K_2SO_4 relative to the binder.
- The xonotlite and wairakite generated in hydration process of FBB.
- These zeolite minerals and C–S–H gels improved strength and water resistance of the paste.
- FBB mortars had good mechanical property and water resistance.
- FBB is an appropriate alternative to PC as a composite cementitious material and can reduce CO_2 emission.

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ABSTRACT

Microstructure and mechanical properties of new binder with high fluorogypsum amount and low Portland cement amount were investigated. The strengths of mortars with fluorogypsum-blast furnace slag-based hydraulic cementitious binder (FBB) were studied at different hydration ages, showing that their later strengths increased rapidly. In 28 days, their compressive strengths, flexural strengths and softening coefficients were all above 59.0 MPa, 10.0 MPa and 0.90, respectively. Microscopic analysis indicated that their hydration products were mainly ettringite, C–S–H gels, xonotlite, dihydrate gypsum crystals, with wairakite generated after 90 days. The generation of zeolite minerals and packing action of filamentous C–S–H gels further improved the strength and water resistance of the paste.

1. Introduction

With the rapid development of infrastructure and increasing demand for residential facilities in many developing countries, the demand for construction materials has also increased rapidly. While Portland cement (PC) has been traditionally used in construction, its production is known to be energy intensive and contributes significantly to worldwide greenhouse gas emissions [1–5]. It is well known that the gypsum is a good alternative environmentally friendly binder material. Increase in the amount of gypsum used in cementitious binder and reduction of PC content are favorable for the reduction of CO_2 emissions and protection of the environment. Every year, large quantities of gypsum, such as phosphogypsum, fluorogypsum and borogypsum, are widely produced as by-products in chemical process industries. Fluorogypsum (FG) is a byproduct of hydrofluoric acid production. In China, production of one ton of HF can produce four to five tons fluorogypsum. Over 400 million tons of fluorogypsum have been generated by 2010. Most of the generated fluorogypsum is transported to waste dumps stacks requiring large amounts of land and harming the environment. Fluorogypsum utilization rate is low except for a small amount of fluorogypsum used as cement retarder [6]; in particular, utilization of fluorogypsum in outdoor applications and in construction is greatly limited because of its low mechanical strength and poor water resistance.

However, fluorogypsum has been shown to exhibit higher potential activity compared with other anhydrites because of its main component known as β-anhydrite [7]. This study focused on the study of utilization of the industry waste residue to improve the hydration activity of fluorogypsum as a cement substitute. The previous studies have shown that the mechanical strength and poor water resistance of fluorogypsum can be improved by mixing with other Si–Al based materials such as blast furnace slag (BFS),

* Corresponding author.
E-mail address: hxq@ctgu.edu.cn (X. Huang).

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fly ash (FA), and metakaolin (MK) [8–13]. Yan studied systems of 31–50% FG, 16–20% PC and 53–64% FA as water-binder of pastes for 0.20–0.35 [8–11] and it was found that the strength of no-slump concrete with this binder was reduced within 180 days [12]. Escalante-Garcia and Fraire-Luna [13] investigated the properties of composite cementitious pastes with 75% FG, 15–25% BFS and 0–15% MK and found that the MK was very reactive and could enhance the strength of pastes since the early times. The compressive strength was found to increase slowly, reaching as high as 14.6 MPa in one year. Moreover, Escalante-Garcia studied the pastes' compressive strength of the binder material based on 50–80% FG, 15–50% PC and 10–15% FA, with the results showing that all pastes compressive strengths reached 32 MPa under water, but decreased when curing under hot and humid condition. Escalante-Garcia further investigated the hydraulic characteristics and stability of binder materials with 50–75% FG, 15–30% PC, 10–20% BFS, 1% superplasticizer and 1–3% different alkaline sulfates relative to the binder and found that only the use of K_2SO_4 was favorable for strength and dimensional stability [14]. Yin and Zhong found that the fluorogypsum activity was enhanced effectively by physical and chemical modifications [15]. Yan [16,17] investigated the effect of fly ash and fluorogypsum on the compressive strength of cement, with the obtained results suggesting that the mortar compressive strength of cementitious composites based on 60% PC, 20% fluorogypsum and 20% FA was 43.9 MPa at 28 days.

A survey of the previous reports discussed above shows that previous studies have concentrated on modifying fluorogypsum by mixing different Si–Al based materials, However, these binders were all composed of 15–60% PC or 10–15% MK as well as other complementary cementitious materials, and the high compressive strengths were attained due to the low water binder content from 0.22 to 0.35 or due to the addition of superplasticizer. It is well known that the general water binder fractions of the C20–C30 grade concretes widely used in China varies from 0.40 to 0.55. In this work, we investigated the fluorogypsum-blast furnace slag-based hydraulic cementitious binder (FBB) composed of 40–50% FG, 45–55% BFS, 5% PC and 1% K_2SO_4 without a superplasticizer. X-ray diffraction (XRD), scanning electron microscopy (SEM), FT-IR and thermogravimetric-differential scanning calorimetry (DSC-TG) analyses were used to reveal the long term hydration and hardening mechanism; additionally, mortar strength studies of this binder all demonstrated the good performance of this material as an alternative binder of PC.

2. Materials and methods

2.1. Materials

The chemical compositions obtained by X-ray fluorescence spectroscopy and FT-IR spectra of raw materials were shown in Table 1 and in Fig. 1, respectively. The pH of original fluorogypsum from the production conveyor was 1.90. In this study, original fluorogypsum was mixed with quicklime to neutralize the acid until pH 8.0, dried and grounded in a ball mill. Its specific gravity, the reduction of 0.08 mm sieve residue and Blaine specific surface area were 2840 kg/m^3, 3.14% and 827 m^2/kg, respectively. Furthermore, the fluoride concentration of FG was 2.4282 mg/L, which was far belower 1 g/L (Chinese standards "Standards for drinking water quality GB5749-2006") and did not harm on the environment and health. XRD data of FG showed $CaSO_4$ peaks and minor phases of calcium fluoride (Fig. 2). The Blaine specific surface area of granulated blast furnace slag (BFS) was 322.0 m^2/kg and the main mineral phase was the glass body composed of calcium–aluminum–silicon-rich compounds (Fig. 3), the reduction of 0.08 mm sieve residue and specific gravity of BFS were 3.72% and 2910 kg/m^3, respectively. The PC phase was composed of 56.2% C_3S, 16.2% C_2S, 5.5% C_3A and 12.5% C_4AF by Rietveld phase quantification methods (Fig. 4). The Blaine's surface area, the reduction of 0.08 mm sieve residue and specific gravity of PC were 386.2 m^2/kg, 4.17%, 3170 kg/m^3, respectively.

2.2. Strength and softening coefficient of mortars test

FBB was composed of 40–50% FG, 5% PC, 45–55% BFS (Table 2) and 1% K_2SO_4 relative to the binder. These samples preparation and strength test of mortar were performed in accordance with the Chinese Standard GB/T 17671-1999, which was the same as the ISO 679:1989 standard. Chinese cement standard sand was used in the test. The sand/binder (s/b) and water/binder (w/b) ratios of the mortar mixtures were kept at 3.0 and 0.50, respectively.

Mortar samples were cast in cuboid molds (40.0 mm width × 40.0 mm thickness × 160.0 mm length). After removal from the molds, all samples were cured under water at 20 ± 1 °C and 95% relative humidity (Rh) for 3, 7, 28, 60, 90 and 180 days. The corresponding pastes were prepared and cured in the same conditions.

The curing was applied to two sets of specimens, the compressive strengths of one set of specimens under water saturation were measured immediately, while another set of samples were placed in a vacuum drying oven at the temperature of 60 °C for 24 h, and then the compressive strengths of the specimens in the dry state were measured. The values of the softening coefficients of the mortars were obtained using Eq. (1):

$$\text{Softening coefficient of mortars} = Q_1/Q_2 \quad (1)$$

Here Q_1 is the compressive strength for water immersion, and Q_2 is the compressive strength for drying conditions.

2.3. Microstructure analysis

The mortar strengths were determined at the scheduled ages. Corresponding pastes were taken and crushed at the same ages and then immersed in absolute alcohol for 48 h to cease further hydration. Fragments of the crushed samples were dried at 60 °C to perform XRD, SEM, FT-IR and TG-DSC tests. XRD analysis of the crushed samples were performed using a Rigaku DIMAX-RB diffractometer with a Cu target. The apparatus used for SEM examination was a scanning electron microscopy. (JSM-5610LV, Jeol). DSC/TG analysis was carried out using a NETZSCH STA 449F3 instrument under air atmosphere. A Nicolet Magna-IR 560 with an insert cell was used as the spectrometer for diffuse reflectance spectroscopy.

Table 1
Chemical compositions of raw materials (wt.%).

	CaO	SiO_2	Al_2O_3	MgO	SO_3	Fe_2O_3	TiO_2	K_2O	CaF_2	CO_2
FG	39.27	0.58	0.16	–	56.7	0.14	–	0.05	1.45	–
BFS	38.65	29.94	15.94	7.98	3.74	1.18	0.65	0.62	–	0.12
PC	65.47	20.02	4.36	1.64	1.92	3.33	0.23	1.27	–	0.77