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Study on the performance of FGD gypsum-metakaolin-cement composite cementitious system

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HIGHLIGHTS

- FGD gypsum was used as water hardening supplementary cementitious component with metakaolin.
- Mortar strength of some samples exceeded the Portland cement after 28 days.
- The volume stability of most tested mortar samples was satisfied.
- In the tested samples with thermally activated FGD gypsum, partial crystal transformation from ettringite to AFm occurred.
- The comparison between the expansion stress and the tensile strength can be used to evaluate the volume stability of composite system.

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ABSTRACT

FGD gypsum is a desulfurization by-product from the steelworks, smelting plants, thermal power stations and so on and its output grows day by day, which means that the resource utilization of FGD gypsum is of economic and social significance. In this paper, FGD gypsum dried at 40 °C and FGD gypsum thermally activated at 800 °C were used as a water hardening supplementary cementitious component, and two series of FGD gypsum-metakaolin-cement composite cementitious systems were prepared. After a series of studies, the following conclusions were obtained: The initial setting time of tested paste samples was longer and their interval between initial setting time and final setting time shortened while mortar fluidity decreased slightly. Early mortar strength of tested samples (to 28 d) was lower than the reference sample (namely Portland cement) and the strength increased obviously and some exceeded the reference sample after 28 days. Hydration products such as AFt and C-A-H existed at the same time from 1 day to 1 year in the samples with dried FGD gypsum and there was still unhydrated gypsum after a year. And crystallization of ettringite and gypsum could take place at the same time and partial crystal transformation from ettringite to AFm occurred from 40 d to 365 d with activated FGD gypsum. The volume stability of tested mortar samples kept in water was satisfied for one year in which ettringite amount was in 13–17% of harden paste and the ettringite content achieved 70–80% of the total ettringite amount at 7 d. Excessive crystallization of gypsum could also have an undesirable effect on the volume stability of harden mortar and mortar strength such as Sample B-5 from 40 d to 120 d. The volume stability of tested samples was good if the expansion stress was lower than the tensile strength.

1. Introduction

FGD gypsum is a kind of industrial by-product derived from the sulfur dioxide emissions which are processed by desulfurization equipment, and a large amount of sulfur dioxide is formed from the steelworks, smelting plants, thermal power stations and various chemical plants in the process of combustion of sulfur containing fossil fuels [1,2]. Unused FGD gypsum is stacked in the natural environment, which causes occupation of land and environment pollution [3]. In Japan, soot materials can be made by FGD gypsum and fly ash and lime, producing strength in the process of consolidation reaction, which are used as pavement subbase or land leveling sand [4]. In Germany, FGD gypsum has gradually replaced the natural gypsum, and in the future it will be completely used to produce gypsum products and cement [5,6]. The comprehensive utilization of FGD gypsum in China started

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later and there is still a big gap compared with foreign countries on the production technology and utilization level. FGD gypsum in China is mainly used for low tech products such as building gypsum, plastering anhydrite and cement retarder, and utilization technology of FGD gypsum is not mature and has not yet formed the scale of industrialization and commercialization [7].

At present, many scholars have begun to focus on FGD gypsum in order to enhance its value. Hongyan Liu, Huisheng Shi, et al. [8] found that the right amount of FGD gypsum increased the compressive strength of specimens and reduced drying shrinkage in slag concrete, which effectively prevented shrinkage crack. According to Liuquan Liu, Zhimin Luo, Dongxu Li, et al. [9], because the FGD gypsum had good gelling properties by 150–300 °C thermal activation, the thermally activated FGD gypsum accelerated the hydration of cement in concrete. Daxing Qian, Li Sun, et al. [10] found that in the FGD gypsum-slag-fly ash- cement composite cementitious system, when the content of desulphurization gypsum was 8%, the early strength was increased by 12% and later strength was also improved. In a study by Yonghua Wu, Yuan Yao, Feng Nan, et al. [11], in the FGD gypsum-fly ash-cement ternary compound cementitious system, the properties of shrinkage and expansion were studied, and the activation of fly ash by FGD gypsum was analyzed. Socrates Ioannou et al. [12] found that with the incorporation of FGD gypsum, in the sulphoaluminate cement – fly ash-FGD gypsum system, compressive strength decreased, and the types and morphology of hydration products cannot be changed by different forms of FGD gypsum. According to Marie Michel et al. [13], the characteristics of slag-gypsum-sulfate aluminum cement system were studied, and the compressive strength of the early and mid period increased with the increase of the amount of gypsum.

At home and abroad, FGD gypsum has been mainly used as cement retarder, or made of those air hardening materials such as gypsum board, block and plaster. However, there is little study about FGD gypsum can be used as a water hardening material. In this paper, FGD gypsum was used as water hardening supplementary cementitious material, the macro and micro properties of FGD gypsum-metakaolin-cement composite cementitious system were studied in order to improve the resource utilization of FGD gypsum and broaden the sources of supplementary cementitious materials in cement concrete.

2. Research content and methods

2.1. Raw materials and treatment

2.1.1. Cement

The 52.5# P.I Portland cement used in the paper was from Nanjing China. Its chemical composition and properties were listed in Tables 2.1 and 2.2.

2.1.2. FGD gypsum

FGD gypsum used in this research was derived from a power plant in Fujian, China. 800 °C thermally activated FGD gypsum was calcined in the DRY-36 high temperature industrial furnace.

(1) Chemical composition

The chemical composition of the FGD gypsum was listed in Table 2.3.

(2) Particle size distribution

The particle size distribution of the FGD gypsum was measured by laser particles distribution instrument. Fig. 2.1(a) and (b) were respectively grain size distribution of the thermally activated and the dried FGD gypsum. Table 2.4 was concentration change of FGD gypsum in water. Table 2.5 was the specific surface area of them.

Fig. 2.1(a) showed that the particle size distribution range of the dried FGD gypsum was relatively narrow. Table 2.4 showed that dissolution of thermally activated FGD gypsum was larger than dried FGD gypsum and the reaction rate was faster, which suggested that the performance of thermally activated FGD gypsum was better. Table 2.5 showed that the particle size of thermally activated FGD gypsum was finer than the dried FGD gypsum.

2.1.3. Metakaolin

Metakaolin used in the tests was from Henan, China. Table 2.6 and Fig. 2.2 were respectively the components and X-ray diffraction results.

Table 2.1
Chemical composition of cement.

Item	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	TiO_2	K_2O
Content/%	61.30	20.8	6.34	3.07	1.03	2.29	0.29	0.85

Table 2.2
Basic properties of cement.

Density/(g·cm^{-3})	Specific surface area/(m^2/kg)	Water requirement of normal consistency/%	Setting time/min		Flexural strength/MPa		Compressive strength/MPa	
			Initial	Final	3 d	28 d	3 d	28 d
3.12	375	26	109	154	6.3	10.0	31.5	63.1

Table 2.3
Chemical composition of the FGD gypsum.

Item	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	MgO	Loss
Content/%	31.6	2.7	0.7	42.4	0.5	1.0	19.2