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Properties of mortars made by uncalcined FGD gypsum-fly ash-ground granulated blast furnace slag composite binder

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ABSTRACT

A series of novel mortars were developed from composite binder of uncalcined FGD gypsum, fly ash (FA) and ground granulated blast furnace slag (GGBFS) for the good utilization of flue gas desulphurization (FGD) gypsum. At a fixed ratio (20%) of GGBFS to the composite binder, keeping consistency of the mortar between 9.5 and 10.0 cm, the properties of the composite mortar were studied. The results show that higher water/binder (W/B) is required to keep the consistency when increasing the percentage of FGD gypsum. No obvious influences of the W/B and content of FGD gypsum on the bleeding of paste were observed which keeps lower than 2% under all experimental conditions tried. The highest compressive and flexural strengths (ratio is 20% FGD gypsum, 20% GGBFS and 60% FA) are 22.6 and 4.3 MPa at 28 days, respectively. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) results indicate that massive ettringite crystals and C–S–H gels exist in the hydration products. At 90 days the mortars with FGD gypsum is dramatically smaller drying shrinkage (563–938 micro strain) than that without FGD gypsum (about 2250 micro strain). The release of the SO_4^{2-} from the mortar was analyzed, indicating that the dissolution of sulfate increases with FGD gypsum. The concentration of SO_4^{2-} releasing from the mortar with 10% FGD gypsum is almost equal to that obtained from the mortar without FGD gypsum. The release of SO_4^{2-} from the mortar with 20% FGD gypsum is 9200 mg·m^{-2}, which is lower than that from the mortar with 95% cement clinker and 5% FGD gypsum.

1. Introduction

In China, ordinary Portland cement (OPC) industry is within the top 10 energy consumption. Driven by the fast development of infrastructure, industry of OPC consumes large amount of energy, emits carbon (Szabó et al., 2006) and pollutes the environment (Yang et al., 2011). To reduce the consumption of OPC, many laboratorial and engineering studies have been proceeding.

One attractive method is partially replacing the OPC by some recycled materials such as Flue gas desulfurization (FGD) gypsum, fly ash (FA) and gypsum ground granulated blast furnace slag (GGBFS). GGBFS has been proved of excellent hydration activity (Austin et al., 1992; Pal et al., 2003) which has been used in many practical constructions. FA is also used in civil engineering (Babu and Nageswara Rao, 1993; Cheerarot and Jaturapitakkul, 2004) even though it has low hydration activity at room temperature (de Vargas et al., 2011).

In 1996, China sets the concentration of SO_2 emitting from power plant is 2100 mg·m^{-3}. The government drives to enforce power plant pollution controls and sets concentration of SO_2 is 400 mg·m^{-3} in 2003. And the concentration of SO_2 is further reduced to 100 mg·m^{-3} by the standard GB 13223-2011 from 2012. Most of power plants are forced to install and use desulphurization equipment obeying the Law of China on the Prevention and Control of Atmospheric Pollution.

FGD gypsum is the by-product of wet flue gas desulphurization process which is employed to reduce SO_2 emissions from power plant to the atmosphere. In China, about 76% electric power is produced from coal in 2009. More than one billion ton of coal brings a large amount of FGD gypsum every year. In views of the resource management, economic and environment-protecting points, exploring the utilization of FGD gypsum is of great significance. The general composition of FGD gypsum is $CaSO_4·2H_2O$ (Tzouvalas et al., 2004). There are mainly two ways to make use of FGD gypsum in the constructions, where one is using as cement retarders (Chandara et al., 2009; Tzouvalas et al., 2004), and the other is to be calcined to produce $CaSO_4·0.5H_2O$ or $CaSO_4$ (Guan et al., 2009; Guo and Shi, 2008).

In this paper, the properties of uncalcined FGD gypsum, FA and GGBFS (FFG) composite mortar was studied. It is a new approach to utilization of FGD gypsum. This kind of binder may find its application in civil engineering as different mortars such as grouting mortars for tail void grouting of shield tunnel and low strength concrete.

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2. Experiment

2.1. Raw materials

Uncalcined FGD gypsum, FA and GGBFS were provided by Baosteel Co., Ltd. The alkalinity of suspension of these raw materials was tested using a pH meter by dispersing 10 g solid samples into 100 g water. The chemical compositions and pH value of FGD gypsum, FA and GGBFS were listed in Table 1. The load of trace substances in GGBFS and fly ash are below the Chinese national standards GB/T 1596-2005 and GB/T 18046-2008.

The powder of uncalcined FGD gypsum was analyzed by laser particle-size analyzer (Malvern, Mastersizer 2000) and field emission scanning electron microscope (FEI Company, Quanta 200 FEG) at an acceleration voltage of 20 kV.

SN-II naphthalene formaldehyde condensate superplasticizer was provided by Shanghai Hualian construction admixture manufactory Co., Ltd and its solid content was 40%. Bentonite was provided by Anqin Company in Zhejiang Province, east of China.

2.2. Specimens preparation and test methods

When the mortar is prepared with sand, FFG binder and water, it shows very pool workability and very large bleeding. To improve the workability and reduce the bleeding, suitable amount of Bentonite and superplasticizer were incorporated in the mortar. The mix proportions of the mortars (Table 2) are as follows if without other specification: the weight ratio of binder to sand was 1:3, bentonite and superplasticizer to binder were 12% and 2%, respectively, and water amount was adjusted to keep the consistency of the mortar in 9.5–10.0 cm. The specimens of $40 \times 40 \times 160$ mm were prepared for test and cured in standard condition (20 °C, relative humidity > 90%) for 7 days and then in room condition (20 °C, relative humidity 60 ± 5%). Bleeding of fresh mortar was tested referring to the Standard GB/T 50080-2002. The water was absorbed with injector till there was no water bleeding. The number of samples is three to generate the average and the relative error of bleeding is below 15%. Consistency and drying shrinkage were tested according to the standard JGJ/T 70-2009. The number of samples of consistency is two and the error is 10 mm. The drying shrinkage was tested from 7 to 90 days which number of samples is three and relative errors are below 20%. The compressive strength and flexural strength of mortar were tested at 3, 7 and 28 days according to the standard GB/T 17671-1999.

The release of SO_4^{2-} from the mortar was studied by the concentration of SO_4^{2-} in the water sample. The water sample was prepared as follow: The specimen of mortar ($40 \times 40 \times 160$ mm) after curing 28 days was marinated in the deionized water (1 L) for a week at 20 °C, then this water was filtered to obtain the water sample. The ratio of surface area of mortar specimen to the volume of water was 28.8 m^{-1}. The concentration of SO_4^{2-} in the water samples was measured by $BaSO_4$ gravimetric analysis. The volume of measured sample is 50 ml, the error is 0.5 mg. The error of concentration is 10 $mg \cdot L^{-1}$.

The specimen for scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis was prepared with the water/binder (W/B) ratio of 0.4, then the paste was cast into the cubic molds of $20 \times 20 \times 20$ mm and cured as described above for mortar specimens. XRD patterns were recorded using a Rigaku International Corporation D/max2550VB3+/PC diffractometer with the Cu Kα radiation (λ = 1.54056 Å) in 2θ ranging from 5° to 65°.

3. Results and discussion

3.1. Size distribution and morphology of uncalcined FGD gypsum

The FGD gypsum dried at 40 °C was characterized by SEM and laser particle-size analysis. It is shown in Fig. 1.The size distribution curve shows two peaks. The small peak (0.1–1 μm) is about 6.7 v% and the large peak (1–400 μm) is about 93.2 v%, respectively. It means there are two types of particle size. The asymmetry of the large peak proves the large particles are non-spheroid. SEM image also shows two types of particle which confirmed the result of laser particle-size analysis. Large tabular particles are gypsum. Gypsum belongs to monoclinic 2/m-prismatic crystal system, which is preferably to form tabular crystallization in the parallelogram and hexagonal direction. So some tabular particles are pseudo-hexagonal. And the tiny ball particles might be FA which was carried by flue gas in the desulphurization process.

3.2. Influence of FGD gypsum on the W/B ratio and bleeding of mortar

The consistency of the fresh FFG mortars is kept between 9.5 and 10.0 cm. The W/B ratio and bleeding are presented in Fig. 2. It shows that the W/B of mortar increases with the increase of FGD gypsum and the decrease of FA. The main reason for this is that the particles of FGD gypsum are tabular shape (Fig. 1) which need more water to reach the same consistency. On the contrary, the abundance of ball-shape particles in the FA (Kutchko and Kim, 2006) improves the contact between the particles which can increases the fluidity of mortar due to the ball bearing effect. On the other hand, the bleeding rate of the fresh mortar doesn't increase with W/B as bentonite can enhance water retention of mortar. The bleeding rate fluctuates between 1.5% and 2.0%. It indicates the workability of the fresh mortar is suitable.

3.3. Compressive strength and flexural strength of the mortars

The values of compressive and flexural strengths are shown in Fig. 3. It can be seen that the FFG mortars present mean values of strength much higher than that of mortar without FGD gypsum. Uncalcined FGD gypsum is mainly consisted of $CaSO_4 \cdot 2H_2O$ (Tzouvalas et al., 2004) which can't be hydrated. However, it is significant to the development of strength.

In all FFG mortars, the compressive and flexural strengths decrease with the increase of FGD gypsum at 3 and 7 days. The highest strength is reached at 10% FGD gypsum and 70% FA at 7 and 28 days. The compressive and flexural strength are 3.1 and 1.4 MPa at 3 days, and 9.7 and 3.2 MPa at 7 days, respectively. The hydration activity of GGBFS is related to alkali. And it is shown that FA is main alkaline raw material in Table 1. It indicates that FA is of key importance to the development of strength at the early days. From 3 to 28 days, the compressive strength of mortars with 20%, 30% and 40% FGD gypsum develops by 13.5 times, 18.4 times

Table 1
Chemical composition of FGD gypsum, FA, GGBFS.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	MnO	TiO_2	SrO	Bound H_2O	Free H_2O	pH
FGD gypsum	4.37	1.73	0.87	29.4	0.64	39.6	0.12				18.1	10.25	7.7
FA	48.9	33.8	5.08	6.49	0.67	0.51	0.88	0.06	1.24	0.19			12.1
GGBFS	33	15.2	0.28	41.3	7.55	1.36	0.29	0.21	0.59	0.09			10.9