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Technical Note

Activation of fly ash–lime systems using calcined phosphogypsum

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Abstract

Experiments were performed to determine the effect of calcined phosphogypsum on the strength of fly ash–lime binders. Significant strength increases compared to binders without calcined phosphogypsum were observed due to the activation. But lowering the lime to calcined phosphogypsum ratio of blends with the same fly ash content yielded a relatively lower compressive development at late ages. Strengths of samples cured first at 45 °C in over 90% R.H. for 12 h and then at room temperature were better than those cured at room temperature all the time. X-ray analysis suggests that the activation of calcined phosphogypsum to the systems was due to the formation of ettringite and dihydrate calcium sulfate during the hydration process.

Keywords: Fly ash–lime systems; Calcined phosphogypsum; Activation

1. Introduction

Large quantities of industrial by-products are produced every year by chemical and agricultural process industries. These materials such as fly ash and phosphogypsum have dual problems of disposal and health hazards. With the more and more wastes being generated, the utilization of fly ash and phosphogypsum is important to save the environment from quick degradation.

The use of fly ash, the major solid industrial waste of coal-fired electric power stations, has been and continues to be the subject of many research studies. Nowadays, fly ash has been increasingly utilized in concrete industry due to the observations that it can lower the heat of hydration, improve the durability and reduce the cost of concrete. In some cases, large volume of fly ash is used to achieve perfect concrete properties. However, one clear disadvantage in the use of most fly ash for cement replacement purposes is that the replacement of cement by fly ash, especially in high volumes, reduces the early strength of concrete significantly. Researchers have found the decrease of early strength is attributed to the slow pozzolanic reactivity between fly ash and calcium hydroxide.

To increase the early strength of the cementitious materials containing fly ash, different approaches are used to accelerate the pozzolanic reaction of fly ash. Among these approaches, chemical activating methods have been widely studied. Chemical methods can be roughly divided into two different types, namely, alkali activation and sulfate activation. The former involved the breaking down of the glass phases in an alkaline environment and the latter is based on the ability of sulfates to react with aluminum oxide in the glass phase of fly ash to produce ettringite that contributes to the early strength [1–3]. With regard to sulfate activation, the use of sodium sulfate and gypsum in dihydrate form had been well studied [4], but use of gypsum in hemihydrate form has been hardly studied.

This work aimed to study the activation of fly ash using hemihydrate calcium sulfate, obtained by calcining phosphogypsum at a temperature of 135 °C. Phosphogypsum, another industrial by-product of phosphoric acid manufacture, consists primarily of $CaSO_2 \cdot 2H_2O$ and contains

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some impurities such as P_2O_5, F^- and organic substances. The presence of impurities puts restrictions on the use of phosphogypsum thus a pretreatment of phosphogypsum is required. The lime in the systems studied in this work just can minimize the adverse effect of the impurities by reacting with the impurities to form series of stable compounds. Blends with different proportions of fly ash, lime and calcined phosphogypsum were prepared and cured at different conditions. The compressive strengths and XRD patterns were obtained to examine whether improvements in the reactivity of fly ash can be obtained by use of calcined phosphogypsum.

2. Experimental

2.1. Raw materials

Fly ash obtained from Guiyang Power Plant was chosen for examination and the phosphogypsum is from Guizhou Wengfu Phosphoric Acid Plant. The chemical composition of the fly ash, lime and phosphogypsum is shown in Table 1.

2.2. Preparation of specimens

Phosphogypsum was calcined at 135 °C for 3 h to obtain hemihydrate calcium sulfate. The calcination process was carried out using an electrical oven. The calcined phosphogypsum was then milled in a roller mill for 8 min before added to the fly ash–lime systems.

Specimens prepared by blending the fly ash, lime and calcined phosphogypsum in different proportions were designated as two groups according to the curing conditions. The range of addition of calcined phosphogypsum was 0–15%.

2.3. Testing of the binders

The blends were mixed in a mechanical mixer and cast into $4.0 \times 4.0 \times 4.0$ cm cubes at normal consistency, and then compacted on a vibrating table. One group of cubes were cured at room temperature, the other were cured first at 45 °C in over R.H. 90% for 12 h and then at room temperature. The curing ages are 1, 3, 7, 28 and 90 days. Compressive strength test was performed on the binders.

Chemical absorption of $Ca(OH)_2$ in samples with the same content of lime and different proportions of calcined phosphogypsum at different hydration times was examined though a chemical analysis method.

XRD patterns of samples were obtained to observe the difference in the hydration products between specimens with and without the addition of calcined phosphogypsum. X-ray diffraction analyses were performed using a D/MAX-III C (40 kV and 50 mA) on a Scintag XDS-2000 diffraction equipped with a graphite monochrometer. Samples being cured at room temperature for 3, 7 and 28 days were used.

Table 1
Chemical composition of fly ash (FA), lime (L) and phosphogypsum (PG)

Constituent (%)	FA	L	PG
$Na_2O + K_2O$	2.21	0.76	0.51
CaO	4.15	69.80	29.05
SiO_2	55.30	3.54	1.25
SO_3	0.31	–	42.19
MgO	1.52	1.97	–
Al_2O_3	23.13	2.11	0.43
Fe_2O_3	5.02	–	0.21
P_2O_5	–	–	3.50
Loss on ignition	2.35	22.58	19.48

3. Results and discussions

3.1. Effect of calcined phosphogypsum on the compressive strength development

The results of the compressive strengths of blends, with or without the addition of calcined phosphogypsum, cured at room temperature and first at 45 °C in over 90% R.H. for 12 h are listed in Tables 2 and 3, respectively. It can be observed that the compressive strengths of binders with calcined phosphogypsum were greatly developed compared with those without calcined phosphogypsum. With the same calcined phosphogypsum content of 8% by mass, there are no obvious differences in the 1 day strengths of all binders, which indicate the hardening of calcined phosphogypsum during the hydration process contributes to the very early strength mostly. But when curing ages reached 3, 7, 28 or 90 days, differences among binders became more and more evident.

Fig. 1 shows that strengths of binders all containing 75% fly ash at 1, 3 and 7 days increased with increases in the addition of calcined phosphogypsum from 0% to 15%, however, the late strengths(after 7 days) developments were relatively lower in samples containing more calcined phosphogypsum. It can be seen from Fig. 2 the increases in the fly ash content from 70% to 85% also led to a decrease in the strengths.

Fig. 3 gives the influence of content of calcined phosphogypsum on the absorption of $Ca(OH)_2$ in the systems. The absorption of $Ca(OH)_2$ after 7 days decreases with increases in the calcined phosphogypsum content. This behaviour can be attributed to the decrease in alkalinity of environment with increase in the ratio of calcined phosphogypsum to lime.

Compared with the results of samples cured at room temperature (Tables 2 and 3, Fig. 4), the strengths at different ages of specimens cured first at 45 °C in over 90% R.H. for 12 h were significantly increased, meaning that the curing conditions also had an influence on the degree of hydration process. It can be observed from Fig. 4 the longer time samples cured at temperature 45 °C in over 90% R.H., the higher strengths they can obtain. An appro-