Influence of autoclaved pretreatment on the properties of phosphogypsum-based composite binders

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Abstract. Phosphogypsum-based composite binder (PGCB) has been made from autoclaved phosphogypsum (PG), fly ash, lime, Portland cement and a chemical activator. The influence of autoclaved pretreatment on the properties of PG and PGCB has been investigated. It was found that the crystalline phases of original PG could be transformed, the impurities of original PG also could be effectively removed by the autoclaved pretreatment process. Under the optimum autoclaved pretreatment conditions (autoclaving at 180 °C for 6 hours), the dry compressive strength of PGCB mortars after 28 days was 31.8 MPa and the ratio of the compressive strength in wet-saturated state to that in dry state (W/D) was 0.59. PGCB mortars show good properties and water resistance with the suitable autoclaved pretreatment.

1. Introduction

Phosphogypsum (PG) is a by-product during the production of fertilizer from phosphate rock with the wet process. Generally, about 5 tons of PG will be generated for producing one ton of phosphoric acid [1], and an annual total production of PG is approximately 280 million tons worldwide. In China, around 50 million tons of PG are produced per year [2], and only 15% of which are recovered [3]. Most of the PG has been stacked. This situation has caused serious environmental impacts [4]. Making rational use of PG is one economic and effective method to control the environmental pollutions. However, the impurities contained in PG restrict the utilization of PG a lot. Therefore, pretreatment processes have been widely applied to modify PG and improve its quality. Potgieter [5] investigated a combined treatment of wet milling PG with lime slurry in a ball mill. Kolver [6] suggested a topochemical extraction process for removing radioactive salts, phosphates and other impurities from original PG. Ren [7] studied the pretreatment of PG by autoclaving under a pressure of 0.12 MPa and at the temperature of 120 °C, then calcining at 400, 500, 600, 700 and 800 °C. In this study, PG was firstly autoclaved at 120 -180 °C for 2-6 hours and then used to make PG-based composite binders (PGCBs). Influence of autoclaved pretreatment processes on the properties of PG and PGCB, especially water resistance, were investigated. Water resistance of PGCBs was evaluated by the ratio of the compressive strength in wet-saturated state to that in dry state (W/D) which is usually used to evaluate the water resistance of a cementitious binder.
2. Experimental

2.1. Raw materials
PG raw materials used in this study was provided by a local phosphoric acid plant in Xiangfan City, Hubei Province. The water content of the raw PG is 22.50 wt%, and CaSO₄·2H₂O content is 87.13 wt% in a dry specimen. The radioactivity analyses of PG were carried out by the Supervision and Inspection Bureau of Building Product Quality in Wuhan. The results are shown as the following: ²⁶⁰Ra of 34.50 Bq·kg⁻¹, ²³²Th of 0.42 Bq·kg⁻¹ and ⁴⁰K of 209.44 Bq·kg⁻¹. The level of radioactivity is much lower than the limit of Chinese standard (GB/T 6566-2001), so the PG samples can be used for production of construction materials.

Fly ash was taken from a local coal-combustion power plant in China. Both lime and ordinary Portland cement (OPC) were locally purchased. The main chemical compositions of the raw materials are listed in Table 1.

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

| Constituents | SiO₂  | CaO   | SO₃  | Al₂O₃ | Fe₂O₃ | MgO   | P₂O₅ | K₂O+Na₂O | F⁻ | LOI   |
|--------------|-------|-------|------|-------|-------|-------|------|-----------|----|-------|
| Original PG  | 7.07  | 28.58 | 39.47| 2.89  | 0.43  | 0.62  | 2.35 | 0.12      | 0.34| 19.08 |
| Fly ash      | 52.50 | 5.68  | 0.50 | 26.28 | 3.60  | -     | -    | -         | -   | 2.20  |
| Lime         | 6.73  | 60.11 | -    | -     | -     | 1.50  | -    | -         | -   | 22.58 |
| OPC          | 20.57 | 58.76 | 2.36 | 5.39  | 2.90  | 3.29  | -    | 0.58      | -   | 4.02  |

2.2. Pretreatment processes and the characterization of PG
The original PG was autoclaved at 120 -180 °C for 2-6 hours, and corresponding PG sample designations are listed in Table 2. The original PG was named PG-0 here, which was obtained by drying the raw PG in an oven at 40 °C. A series of PG-A samples mean the autoclaved the original PG samples in an autoclave with steam under the different pressure of 0.1-0.8 MPa, and at the temperature of 120-180 °C for 2-6 hours. All the PG samples were separately milled by a planetary ball mill until over 85 wt% of particles were in a size of less than 80 μm.

The amounts of impurities (mainly phosphate and fluoride) in PG-0 and pretreated PG samples were determined. Phosphate levels of PG (original/pretreated) samples were measured using the quinoline phosphomolybdate gravimetric method following the Chinese standard (GB/T1871.1-1995). Fluoride was determined according to the Chinese standard (GB/T1872-1995).

Table 2. Sample designation of PG sample, PGCB mortar and PGCB paste

| PG sample | PGCB mortar | PGCB paste | Pretreatment process for PG samples |
|-----------|--------------|------------|-----------------------------------|
| PG-0      | M-0          | P-0        | drying the raw PG in an oven at 40 °C |
| PG-A-120-2| M-120-2      | P-120-2    | Autoclaving at 120 °C for 2 hours  |
| PG-A-120-4| M-120-4      | P-120-4    | Autoclaving at 120 °C for 4 hours  |
| PG-A-120-6| M-120-6      | P-120-6    | Autoclaving at 120 °C for 6 hours  |
| PG-A-140-2| M-140-2      | P-140-2    | Autoclaving at 140 °C for 2 hours  |
| PG-A-140-4| M-140-4      | P-140-4    | Autoclaving at 140 °C for 4 hours  |
| PG-A-140-6| M-140-6      | P-140-6    | Autoclaving at 140 °C for 6 hours  |
| PG-A-160-2| M-160-2      | P-160-2    | Autoclaving at 160 °C for 2 hours  |
| PG-A-160-4| M-160-4      | P-160-4    | Autoclaving at 160 °C for 4 hours  |
| PG-A-160-6| M-160-6      | P-160-6    | Autoclaving at 160 °C for 6 hours  |
| PG-A-180-2| M-180-2      | P-180-2    | Autoclaving at 180 °C for 2 hours  |
| PG-A-180-4| M-180-4      | P-180-4    | Autoclaving at 180 °C for 4 hours  |
| PG-A-180-6| M-180-6      | P-180-6    | Autoclaving at 180 °C for 6 hours  |

All PG samples were immersed into ethanol for 24 hours to terminate the hydration reaction. Subsequently, these samples were dried in an oven at 40 °C. In order to compare with the original PG, the pretreated PG samples were analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM). XRD investigations were carried out with an X'Pert PRO diffractometer (PANalytical B.V.) using Cu Kα, operated at 40 kV. SEM analysis was carried out with a Sirion200 scanning microscope after the samples were coated with gold.
2.3. Preparation and testing of PGCB mortars
The PGCBs were prepared by intimately blending 52 wt% PG with 33 wt% fly ash, 10 wt% OPC, 3 wt% lime and 2 wt% a suitable chemical activator followed by grinding in a ball mill. The mass ratio of binder to sand was 1:3, and the mass ratio of binder to water was 2:1. PGCB mortars were molded with a 40mm × 40mm × 160mm steel mold and set for 24 hours. After de-molding, these mortars were cured for 28 days in ambient air at room temperature of 20±5 °C. Six PGCB mortars for each designation were divided into two groups for performance testing after being cured for 28 days.

Three mortars of the first group were dried in an oven at 40±1 °C until they reached a constant weight. These dried mortars were used to test the dry strength with the method described in the Chinese standard (GB/T 17671-1999). Three mortars of the second group were immersed in water until saturation, and these mortars were tested for saturated strength. The ratio of the compressive strength in wet-saturated state to that in dry state (W/D) was used to evaluate the water resistance of CBPG mortars after normally curing at 28 days. The evaluating parameter (W/D) was calculated by the Equation (1):

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\text{W/D} = \frac{\text{Compressive strength in wet - saturated state}}{\text{Compressive strength in dry state}}
\]  

2.4. Preparation and the characterization of PGCB pastes
The PGCB pastes were simultaneously prepared and cured in the ambient air at room temperature of 20±5 °C. Three group experiments were designated as P-180-2, P-180-4, P-180-6, respectively. Typical PGCB pastes were crushed and grinded after 28 days of curing. The samples were immersed and saturated in ethanol for 24 hours, then dried at 40°C until they reached the constant weight. The crystalline phases of PGCB pastes were analyzed by XRD (XPert PRO), and morphologies of hydration products were investigated by SEM (Sirion200) after the samples were coated with gold.

3. Results and discussion

3.1. Comparison of crystalline phase and morphology between the original and autoclaved PG
XRD pattern of the original PG is shown in Figure 1. XRD patterns of the autoclaved PG samples at 120 - 180 °C for 2 - 6 hours are shown in Figures 2 - 5. Sample PG-0 mainly showed the crystal of dihydrate (CaSO₄·2H₂O). In autoclaved samples, dihydrate (CaSO₄·2H₂O) is still the main crystal. With increasing autoclaving temperature and time, a trace of hemihydrates (CaSO₄·0.5H₂O) crystal appeared. As the autoclave temperature increased to 180 °C, all gypsum phases transformed into anhydrite (Samples PG-A-180). Quartz phase (SiO₂) exists in all types of PG samples as a common inert impurity.

SEM images of the samples are shown in Figure 6. Original PG particles were irregular agglomerates and rhombic crystals, and a large number of granular and flocculent aggregates were attached to the surface of PG crystal, as shown in Figure 6 (a). Morphologies of autoclaved PG samples were significantly different from the morphologies of original PG. The microstructure of PG-A-120-4 appeared a shape of plate crystal, shown in Figure 6 (b). In sample PG-A-140-4, the phosphogypsum crystals began to transform from the plate to the short column, forming less regular columnar crystals, shown in Figure 6 (c). Morphology of PG-A-160-4 appeared a shape of dense columnar crystalline, which is a typical morphology of α-CaSO₄·0.5H₂O. In sample PG-A-180-4, prismatic crystals binding the smaller anhydrite grains were formed, shown in Figure 6 (e).
Figure 1. XRD pattern of original PG sample.

Figure 2. XRD patterns of PG-A-120 samples.

Figure 3. XRD patterns of PG-A-140 samples.

Figure 4. XRD patterns of PG-A-160 samples.

Figure 5. XRD patterns of PG-A-180 samples.
3.2. Impurities of autoclaved PG

The impurities, especially water soluble P\textsubscript{2}O\textsubscript{5} and fluoride, play an important role in the quality of the final PG products. They significantly influence the setting time and strength of PG building materials [8]. Therefore, the impurity contents of original PG and autoclaved PG samples were quantitatively determined. The measured results of total P\textsubscript{2}O\textsubscript{5}, total fluoride, water soluble P\textsubscript{2}O\textsubscript{5} and water soluble fluoride are shown in Table 3. It can be seen that the levels of impurities decreased significantly after autoclaved pretreatment processes when compared to the original PG. The impurities decreased with an increase in autoclave temperature and time, especially water soluble P\textsubscript{2}O\textsubscript{5}. For Sample PG-A-180-4, the water soluble P\textsubscript{2}O\textsubscript{5} was decreased from 1.40 wt% as in the original PG to 0.06 wt%. Therefore, the PG could be effectively purified by the autoclaved pretreatment processes.
Table 3. The content of the impurities in PG samples (wt%).

| PG sample | water soluble P_2O_5 | total P_2O_5 | Water soluble fluoride | Total fluoride |
|-----------|----------------------|-------------|------------------------|---------------|
| PG-0      | 1.40                 | 2.35        | 0.110                  | 0.34          |
| PG-A-120-2| 0.35                 | 1.52        | 0.009                  | 0.37          |
| PG-A-120-4| 0.28                 | 1.31        | 0.012                  | 0.37          |
| PG-A-120-6| 0.22                 | 1.33        | 0.006                  | 0.08          |
| PG-A-140-2| 0.23                 | 1.32        | 0.005                  | 0.07          |
| PG-A-140-4| 0.26                 | 1.52        | 0.005                  | 0.09          |
| PG-A-140-6| 0.29                 | 1.40        | 0.008                  | 0.10          |
| PG-A-160-2| 0.18                 | 1.35        | 0.006                  | 0.11          |
| PG-A-160-4| 0.36                 | 1.55        | 0.005                  | 0.10          |
| PG-A-160-6| 0.19                 | 1.24        | 0.003                  | 0.12          |
| PG-A-180-2| 0.18                 | 1.22        | 0.005                  | 0.14          |
| PG-A-180-4| 0.06                 | 1.05        | 0.004                  | 0.07          |
| PG-A-180-6| 0.07                 | 1.17        | 0.004                  | 0.06          |

3.3. The properties of PGCB mortars

The dry compressive strength and the wet-saturated compressive strength of PGCB mortars after curing for 28 days are shown in Figure 7 and 8. The traditional water resistance evaluating parameter (W/D) of CBPG mortars are plotted in Figure 9. Generally, the dry strength and the wet-saturated strength significantly increased with an increase in the autoclave temperature and time. The wet-saturated compressive strength is commonly lower than the dry strength. Results indicate that the maximum strength of M-180-6 mortar was achieved when the PG was autoclaved at 180°C for 6 hours. However, W/D of M-0 mortar was higher than most of PGCB mortars made from autoclaved PG.

Figure 7. The dry compressive strength of PGCB mortars after curing for 28 days.
3.4. **The hydration and the hydration products of PGCB**

The XRD patterns of P-180 pastes cured for 28 days are shown in Figure 10. Ettringite and C-S-H gel are the hydrated products that contribute to the strength of the specimens. Quartz and mullite are the main components in the un-reacted fly ash, which could contribute to an increase in the long-term strength. The hydration of new gypsum phase after pretreatment also contributed to the strength. In the mean time, with the increase of the autoclaving time at 180 °C, the peaks of ettringite and C-S-H were stronger, which is consistent with the results of the strength tests.

The SEM image of P-180-6 paste cured for 28 days is shown in Figure 11. A significant amount of euhedral ettringite needles were coated with partially hydrated fly ash spheres. Ettringite and C-H-S made the PG and fly ash particles connect with each other and formed the skeleton structure, which made the structure more hardened and improved the strength and water resistance of PGCB pastes.
4. Conclusions
The autoclaved pretreatment has a strong influence on the crystalline phase of PG. Dihydrate (CaSO$_4$·2H$_2$O) is the main crystalline phase of the PG samples when they are autoclaved at 120-160 °C, a trace of hemihydrates (CaSO$_4$·0.5H$_2$O) crystal formed with increasing autoclaving temperature and time. As the autoclave temperature increased to 180 °C, all of gypsum phase is transformed into anhydrite. Moreover, the autoclaved pretreatment also can effectively purify the PG samples. Especially, total fluoride, water soluble fluoride and water soluble P$_2$Os could be almost removed when PG samples are autoclaved at 120-180°C.

When the autoclaved PG was used as one ingredient to prepare M-180-6 mortar, the maximum strength of M-180-6 mortar was achieved when the PG was autoclaved at 180°C for 6 hours. The dry compressive strength and the wet-saturated compressive strength of M-180-6 mortars after curing for 28 days are 31.8 MPa and 19.4 MPa respectively. W/D of M-180-6 mortars after curing for 28 days is 0.59. XRD and SEM analysis further showed that dehydrate, ettringite and C-S-H gel were the main hydration products. Dihydrate contributes to the early strength. Both ettringite and C-S-H gel contribute to not only the early strength but also the later strength. These products coat the surfaces of fly ash and PG, and may improve the water resistance of CBPG mortars.

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