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

School of Environmental Science and Engineering, Huazhong University of Science & Technology, Wuhan 430074, China

ABSTRACT: Phosphogypsum-based composite binder (PGCB) is made from phosphogypsum (PG), fly ash, lime, Portland cement, and chemical activator. The influence of pretreated PG on the properties of PGCB was investigated. Three types of pretreatment processes were conducted on PG, i.e. autoclaving at 180 °C for 4 hours, calcining at 700 °C for 2 hours, and autoclaving at 120 °C for 1.5 hours followed by calcining at 700 °C for 2 hours. The crystalline phases could be transformed and the impurities of original PG could be effectively purified by the pretreatment process. Weight loss after static water attack (WLSW) and weight loss after flowing water attack (WLFW) of the PGCB mortars were studied to evaluate their water resistance. Effects of the content of pretreated PG on the properties of the PGCB were investigated. An optimum proportion, 80% of the pretreated PG content, was initially proposed. At the optimum proportion, the compressive strength of PGCB mortars after the tests of WLSW and WLFW could keep more than 30 MPa, and WLSW and WLFW were lower than 0.5% and 2% respectively. Generally PGCB mortars showed good water resistance after PG was pretreated with a suitable process.

Keywords: phosphogypsum-based composite binder, pretreatment process, purification, water resistance, waste management

1 INTRODUCTION
Phosphogypsum (PG) is a by-product in the production of fertilizer from phosphate rock with the wet process. Generally, about 5 tons of PG generate in the production of per ton phosphoric acid (Tayibi et al., 2009), and an annual total production of PG is approximately 280 million tons worldwide (Yang et al., 2009). In China, around 40 million tons PG are produced per year, and only 10% of them are recovered (Huang and Lin, 2010). Most of the PG has been stacked. This situation has caused serious environmental impacts (Reijnders, 2007).

The construction and building industry is a major possible consumer of the PG. However, the impurities contained in PG restrict the use of PG in building materials. They have adverse effects on setting and hardening of binders (Singh, 2003) Therefore, pretreatment processes are widely used to reduce the negative effects of these impurities. Potgieter (2003) investigated a combined treatment of wet milling PG with lime slurry in a ball mill. Singh (1996) conducted a purification process for PG by wet sieving with a 300-micron sieve and a hydrocyclone. Based on the results, a pilot plant with a capacity of one ton per shift was proposed. Kolver (2004) suggested a topochemical extraction process for removing radioactive salts, phosphates and other impurities from original PG. Smadi (1999) studied the pretreatment of PG by calcining at temperatures of 170, 600, 750, 850, and 950 °C. The pretreated PG used in the mortar substituting part of Portland cement and the maximum strength was found to be for PG calcined at temperatures of 850 and 900 °C.
Although some researchers reported that PG could be used for preparation of building materials after treatment, there are numerous challenges of the application of PG in the construction materials, i.e. cost, radioactivity, the public acceptance and water resistance etc. Among which, water resistance is considered as one of the important properties of building materials in an environment of rich-humidity or water-attacking, especially for cementitious binders containing gypsum (Kovler, 1998). In this study, PG-based composite binders (PGCBs) were prepared from PG that had gone through different pretreatment processes. Influence of pretreatment processes on the properties of PGCBs, especially water resistance, was investigated. The ratio of the compressive strength in wet-saturated state to that in dry state (W/D) is usually used to evaluate the water resistance of a cementitious binder. However, studies on how to evaluate weight loss and strength after the static water attacking and flowing water attacking are rare in the previous literatures. In this study, weight loss after static water attack (WLSW) and weight loss after flowing water attack (WLFW) of the PGCB mortars were studied to evaluate their water resistance.

2 EXPERIMENTAL

2.1 Raw materials

The raw materials of PG used in this study were provided from a local phosphoric acid plant in Xiangfan City, Hubei Province. The water content of the raw PG is 22.50% (by wt.), and CaSO₄·2H₂O content is 87.13% (by wt.) in a dry specimen (drying at 40 °C). 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: 226Ra 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 purchased locally. The chemical compositions of main raw materials are listed in Table 1.

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

2.2 Pretreatment processes and test methods for PG

Three types of pretreatment processes were conducted on PG, 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. PG-A was autoclaved by placing the raw PG in an autoclave with steam under the pressure of 0.8 MPa and at the temperature of 180 °C for 4 hours. PG-C was obtained by calcining PG-0 at 700 °C for 2 hours in a muffle furnace. PG-AC was obtained by autoclaving the PG at 120 °C for 1.5 hours followed by calcining at 700 °C for 2 hours in a muffle furnace. All the PG samples were milled separately 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 the original and pretreated PG samples were determined. Phosphate levels of PG (original and pretreated) samples were
measured using the quinoline phosphomolybdate gravimetric method following the Chinese standard (GB/T 1871.1-1995). Fluoride was determined in accordance with the Chinese standard (GB/T 1872-1995).

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

<table>
<thead>
<tr>
<th>PG sample</th>
<th>PGCB mortar</th>
<th>PGCB paste</th>
<th>Pretreatment process for PG samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG-A</td>
<td>M-A</td>
<td>P-A</td>
<td>Autoclaving under a pressure of 0.8 MPa at 180 °C</td>
</tr>
<tr>
<td>PG-C</td>
<td>M-C</td>
<td>P-C</td>
<td>Calcining at 700 °C</td>
</tr>
<tr>
<td>PG-AC</td>
<td>M-AC</td>
<td>P-AC</td>
<td>Autoclaving the PG at 120 °C for 1.5 hours followed by calcining at 700 °C</td>
</tr>
</tbody>
</table>

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 XPert PRO diffractometer (PANalytical B.V.) using Cu Kα, operated at 40 kV. SEM analysis was carried out with a Sirion 200 scanning microscope after the samples were coated with gold.

2.3 Preparation and testing of PGCB mortars

The mix proportions of PGCB are listed in Table 3. The three groups were designated as M-A, M-C, and M-AC, respectively, listed in Table 2.

Table 3 Proportions of PGCB (%)

<table>
<thead>
<tr>
<th>PG</th>
<th>Fly ash</th>
<th>Lime</th>
<th>Portland cement</th>
<th>Chemical activator</th>
</tr>
</thead>
<tbody>
<tr>
<td>60.0%</td>
<td>27.0%</td>
<td>3.0%</td>
<td>10.0%</td>
<td>2.0%</td>
</tr>
<tr>
<td>70.0%</td>
<td>17.0%</td>
<td>3.0%</td>
<td>10.0%</td>
<td>2.0%</td>
</tr>
<tr>
<td>80.0%</td>
<td>7.0%</td>
<td>3.0%</td>
<td>10.0%</td>
<td>2.0%</td>
</tr>
<tr>
<td>90.0%</td>
<td>0.0%</td>
<td>3.0%</td>
<td>7.0%</td>
<td>2.0%</td>
</tr>
<tr>
<td>100.0%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>2.0%</td>
</tr>
</tbody>
</table>

The mixtures were blended 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 40 mm × 40 mm × 160 mm 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. Nine PGCB mortars for each designation were divided into three groups for performance testing at 28 days of curing.

Three mortars of the first group were dried in an oven at 40 ± 1 °C until they reached constant weight. These dried mortars were used to test the dry strength with the method described in the Chinese standard (GB/T 17671-1999).

Moreover, weight loss after static water attack (WLSW) and weight loss after flowing water attack (WLFW) were respectively used to evaluate the water resistance of the PGCB mortars after 28 days of curing according to the method suggested by Chen et al. (2003).

Three mortars of the second group were dried in the oven at 40 ± 1 °C until they reached constant weight, then immersed 30 days in a static water bath and finally dried in the oven at 40 ± 1 °C until constant weight again. In the mean time, the dry weights of each mortar before and after immersion were measured, and recorded as W_1 and W_2 respectively. Both weights were used in the calculation of WLSW as in Equation (1):
\[ W_{LSW} = \frac{W_1 - W_2}{W_1} \]  
(1)

Three mortars of the third group were dried in the oven at 40 ± 1 °C until they reached constant weight, then immersed 10 days in a flowing water bath with a flow rate of 2800 ml·min\(^{-1}\), and finally dried in the oven at 40 ± 1 °C until constant weight again. In the mean time, the dry weights of each mortar before and after immersion were measured, and recorded as \( W_1 \) and \( W_3 \) respectively. Both weights were used in the calculation of WLFW as in Equation (2):

\[ WLFW = \frac{W_1 - W_3}{W_1} \]  
(2)

Then the strength of PGCB mortars after static or flowing water attack was tested.

2.4 Preparation and testing 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-A, P-C, and P-AC, respectively, as listed in Table 2. The PGCB pastes were used to investigate hydrate products and morphologies of hydration products by XRD and SEM. Typical PGCB pastes (P-A) 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 constant weight. The crystalline phases of PGCB pastes were analyzed by XRD (X’Pert PRO), and morphologies of hydration products were investigated by SEM (Sirion 200) after the samples were coated with gold.

3 RESULTS AND DISCUSSION

3.1 Comparison of crystalline phase and morphology between original and pretreated PG

XRD patterns of original PG and pretreated PG samples are shown in Fig. 1. Sample PG-0 has the main crystal of dihydrate (\( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \)). However, in Sample PG-A, PG-C and PG-AC, anhydrite (\( \text{CaSO}_4 \)) is the main crystal. Quartz phase (\( \text{SiO}_2 \)) exists in all types of PG samples as a common inert impurity.

![XRD patterns of PG samples.](image)

Figure 1. XRD patterns of PG samples.
SEM images of samples are shown in Fig. 2. Original PG particles were irregular agglomerates and rhombic crystals, as shown in Fig. 2(a). Morphologies of pretreated PG samples are significantly different from the morphologies of original PG. The microstructure of PG-A appears a shape of plate crystal, shown in Fig. 2 (b). In sample PG-C, prismatic crystals binding the smaller anhydrite grains are formed, shown in Fig. 2 (c). The result corroborates the findings of Singh and Garg (2000). Morphology of PG-AC shows appearance of rectangular crystals with a coarse surface, which is the characteristics of the anhydrite as a result of calcined products from $\alpha$-CaSO$_4\cdot0.5$H$_2$O, shown in Fig. 2 (d).

3.2 Impurities of pretreated PG

The impurity contents of original PG and pretreated PG samples were quantitatively determined. The results are shown in Fig. 3.

Figure 2. SEM images of PG samples (a) PG-0, (b) PG-A, (c) PG-C, and (d) PG-AC.

Figure 3. The content of the impurities in PG samples.
As shown in Fig. 3, the contents of the soluble phosphorus and water soluble fluoride decreased significantly after the pretreatment processes when compared to the original PG. Therefore, the PG could be effectively purified by the pretreatment processes.

3.3 Water resistance of PGCB mortars

The strengths of PGCB mortars after static or flowing water attacking compared with the dry strength at 28 days of curing are shown in Fig. 4. Strengths of PGCB mortars were apparently improved in PG-fly ash-OPC-lime system when compared to 100% PG. Moreover, different pretreatment processes showed different effects on water resistance under static or flowing water attacking. The compressive strengths of M-A mortars after WLFW and WLSW were significantly lower than the corresponding dry strengths with the different content of PG from 60% to 100%. The compressive strength of M-C and M-AC mortars after WLFW and WLSW were higher than (or near) the corresponding dry strengths when the content of PG was lower than 80%. It indicated that M-C and M-AC mortars showed better water resistance than M-A mortars. The optimum amount of the pretreated PG content was 80%. At this optimum proportion, the compressive strength of M-C and M-AC mortars after WLFW or WLSW could keep more than 30 MPa.

![Figure 4. Compressive strengths of PGCB mortars.](image)

Weight losses of PGCB mortars after flowing or static water attacking are plotted in Fig.5. The WLFW of different pretreated PGCB mortars did not change markedly with the content of pretreated PG varied in the range of 60%-90%, but thereafter the WLFW increased drastically. The WLSW of different pretreated PGCB mortars did not change significantly in the range of 60%-80% pretreated PG, but thereafter increased sharply. The PGCB mortars made from 80% pretreated PG showed best water resistance, and its WLFW and WLSW were lower than 2% and 0.5% respectively. Generally, the optimum amount of the pretreated PG content was 80% by considering lower WLFW and WLSW, which was consistent with the results of the compressive strengths in Fig. 4. When the content of pretreated PG varied from 60% to 80%, the WLFW and WLSW of M-A were higher than those of M-C and M-AC. It indicated that M-C and M-AC mortars showed better water resistance than M-A mortars.
3.4 The hydration and the hydration products of PGCB

The XRD patterns of P-A pastes cured for 28 days are shown in Fig. 6. Ettringite (AFt) was the hydrated products that contributed to the strength of the specimens. Quartz and mullite were the main components in the un-reacted fly ash, which could contribute to an increase in the long-term strength. In the mean time, with the increase of the content of PG-A, the peaks of mullite were weaker. The new dihydrate phase also contributed to the strength. When the content of PG-A was 80% or 90%, some anhydrites which did not transform completely were still identified in PGCB pastes. The calcium hydroxide was the hydration product of OPC and the lime.
The SEM image of P-A paste with the content of PG-A of 80% at the 28 days of curing is shown in Fig. 7. The hydrated agglomerates were engulfed by a significant amount of euhedral ettringite needles. Ettringite 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

An optimum content of the pretreated PG in PGCB is 80% by considering compressive strength and weight loss after static water or flowing water attacks. At this optimum proportion, WLSW and WLFW are lower than 0.5% and 2% respectively, and the compressive strength of M-C and M-AC mortars after tests of WLFW or WLSW could keep more than 30 MPa.

Different pretreatment processes showed different effects on water resistance under static or flowing water attacks. When the content of pretreated PG varied from 60% to 80%, the WLFW and WLSW of M-A were higher than those of M-C and M-AC. In general, M-C and M-AC mortars showed better water resistance than M-A mortars.

XRD and SEM analysis showed that the dihydrate and ettringite were the main hydration products. Both ettringite and dihydrate could contribute to the strength of PGCB mortars. These products coated the surfaces of hydrated agglomerates, and could improve the strength and water resistance of PGCB mortars.

ACKNOWLEDGEMENTS

The authors would like to thank for the funding support of solid waste recycling projects from New Century Excellent Talents Project of Ministry of Education (NCET-09-0392). The authors also would like to thank Analytical and Testing Center of Huazhong University of Science and Technology for providing the experiment facilities.

REFERENCES


