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Low cost and high efficiency utilization of hemihydrate phosphogypsum: Used as binder to prepare filling material

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HIGHLIGHTS

- The hemihydrate phosphogypsum (HPG) modified by quicklime was used as filling binder (HCM).
- The HCM achieved low cost and efficient utilization of HPG.
- The filling material (HFM) mixed by HCM and tailings was suitable for various mining methods.
- The HFM had enough long-term strength and good stability under humid environment.

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ABSTRACT

With the gradual application of hemihydrate-wet process, the comprehensive utilization of hemihydrate phosphogypsum (HPG) needs to be concerned by phosphorus chemical industry. In order to utilize HPG and control goafs in mine, HPG was used to prepare low-cost filling binder (HCM) in the work. The flexural and compressive strength for 2 h of HPG neutralized by 1.5% quicklime was 1.6 MPa, 3.2 MPa, respectively, which can meet the strength requirements of filling binder. Quicklime can shorten the setting time of HCM and improve its early strength. The HCM neutralized by 1.0–1.5% quicklime had the best strength and its dry compressive strength for 3 days reached 16.0 MPa. The compressive strength of filling body mixed by HCM and the addition of 0–160% tailings (HFM) can meet various mining methods. Moreover, the tailings improved the mine filling adaptability of HFM, and the strength loss coefficient of HFM soaked for 240 days was only 0.25. In humid environment, although the compressive strength of HFM decreased as the curing time extended, it will gradually stabilize.

1. Introduction

Dihydrate-wet and hemihydrate-wet process are the main phosphoric acid production methods, the chief by-products of which are dihydrate phosphogypsum (referred to as phosphogypsum, PG) and hemihydrate PG (HPG), respectively [1]. As we all know, PG, the main phase of which is $CaSO_4{\cdot}2H_2O$, cannot form a solidified body without heat treatment. By contrast, HPG is mainly composed of $CaSO_4{\cdot}0.5H_2O$, which presents better self-hardening properties during $CaSO_4{\cdot}0.5H_2O$ converting to $CaSO_4{\cdot}2H_2O$.

At present, dihydrate-wet process plays a leading role in the phosphorus chemical industry. The annual PG production is about 50 million tons and the surface stockpile is more than 200 million tons in China [2]. Meanwhile, the soluble impurities in PG such as residual acids, fluorides will deteriorate the properties of PG products and limit the application scope of PG [3–5]. Traditionally, the PG is prepared into building materials by calcination, autoclaving or semi-dry process, which make the PG dehydration and further conversion into HPG [6–8]. However, in the most of above studies, PG has low consumption and high cost of dehydration.

In order to reduce the high cost of PG dehydration, some efforts have been made on the use of original PG. Yang et al. [9] utilized the original PG to prepare the non-autoclaved aerated concrete. Tian et al. [10] used the original PG as raw material to prepare foam concrete. In the study of Yang et al. [11], the original PG was used to prepare self-leveling mortar, and the innovative mortar cost has been greatly reduced due to the addition of PG. These efforts not only cut down the PG use cost but also improved its reuse proportion.

The particle size of phosphate ore can be coarser and the direct concentration of phosphate acid is nearly doubled, which makes

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the economic benefits of hemi-wet process better than the dihydrate-wet process [12–14]. With the increasing demand for high-quality phosphoric acid in the modern phosphorus chemical industry, hemi-wet process will be one of the main wet process [14,15]. Therefore, low-cost and large-scale processing technologies are also needed to consume HPG.

Some fields, such as mining, road construction, etc. can consume a lot of engineering materials and are not strict in the strength and source of the materials. In this study, original HPG, without any treatment, was innovatively directly used to prepare cementitious material (HCM) applied to mine filling. Studies have shown that quicklime can significantly improve the HPG hydration performance by neutralizing soluble acid impurities [10,16], so quicklime should be the main raw material of HCM. Compared with PG products, HCM took full advantage of the self-hardening characteristics of HPG, providing a simple, low-cost and high-consumption HPG utilization way. Moreover, tailings, from ore dressing process, are one of the main wastes in the phosphorus chemical industry. Adding tailings in HCM not only protects the environment, but also reduces the material cost and improves its mine filling adaptability.

The paper analyzed the effect of quicklime on HCM properties and the characteristics of HCM. Then the tailings used as inert material were binded by HCM to prepare filling material (HFM). The strength stability of HFM under standard and soaking conditions was evaluated by long-term strength and strength loss coefficient. The curing mechanism of HCM was studied based on laboratory test and theoretical analysis. Finally, the advantages of HFM were compared with cement-based filling material (CFM).

2. Experimental

2.1. Raw materials

HPG, quicklime, tailings, α-hemihydrate gypsum (α-HG) and β-hemihydrate gypsum (β-HG) were used in this work. HPG and tailings were taken from phosphate fertilizer plant in Guizhou Province, China, with water content of 20.3% and 11.5%, respectively. The quicklime containing 77.4% effective calcium and α-HG were commercially available. β-HG was prepared from PG by the stir-frying technology. The chemical compositions of HPG and tailings were shown in Table 1. The HPG contained 5.4% crystal water and its pH was 3.4 due to the presence of 0.42% soluble P_2O_5 (SP) and 0.25% soluble fluoride (SF). The SP and SF in tailings can be ignored. The particle size distribution of HPG and tailings were shown in Fig. 1, which indicated that the mean particle size (d_{50}) and uniformity coefficient (C_u) of HPG and tailings were 59.6 μm, 27.8 μm and 3.23, 21.93, respectively. Moreover, 42.63% tailings particles were finer than 20 μm. HPG belonged to homogeneous material and uneven tailings had good gradation as described in the Chinese standard (TB 10001-2005) [17]. The X-ray diffraction (XRD) of HPG and tailing were shown in Fig. 2. HPG contained a small amount of anhydrous gypsum, which was responsible for the HPG crystal water less than 6.2% in theory.

2.2. Mix proportions and preparation process of HCM and HFM

As shown in Table 2, fifteen mix proportions were designed. The plasters of A1-A3 were used to study the properties of α-HG, β-HG and HCM. The plasters of B1-B6 were used to investigate the effects of quicklime content of 0, 0.5%, 1.0%, 1.5%, 2.0%, and 2.5% on HCM's properties and the results provided basis for quicklime content in HFM. The mixtures of C1-C8 were aimed to prepare HFM for different mining methods when the addition of tailings was 20%, 40%, 60%, 80%, 120% and 160%, respectively.

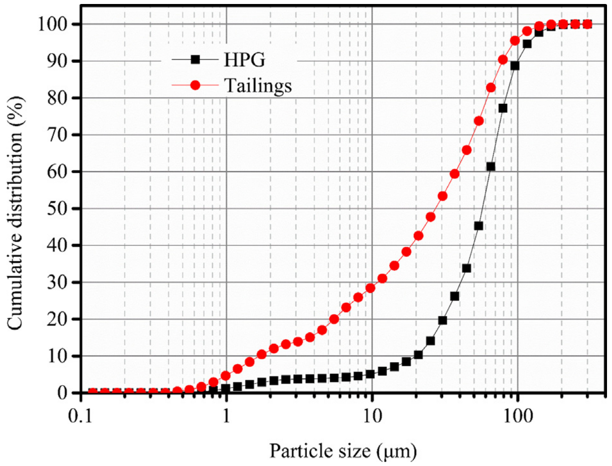

Fig. 1. Particle size distribution of HPG and tailings.

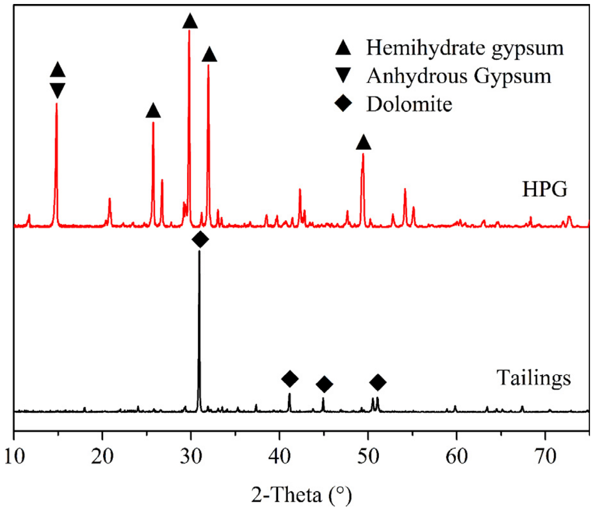

Fig. 2. XRD patterns of HPG and tailings.

2.3. Test methods

According to Table 2, the HCM plasters and HFM mixtures were prepared. Firstly, HPG and quicklime was weighed and pre-stirred for 60 s in a mixer, and then water or tailings was added to the mixer to stir again for 90 s. After the plasters and mixtures were evenly mixed, the water demand of normal density, setting time, and fluidity were determined and the specimens used for strength determination were cast.

Table 1
Chemical compositions of HPG and tailings (wt%).

Compositions (%)	CaO	Al_2O_3	SiO_2	MgO	Fe_2O_3	SO_3	SrO	P_2O_5
HPG	37.86	0.46	4.20	0.28	0.45	44.82	0.36	1.37
Tailings	34.44	0.38	2.59	17.91	0.42	0.82	0.19	6.45