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A novel Two-step Hydration Process of preparing cement-free non-fired bricks from waste phosphogypsum

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HIGHLIGHTS

- A novel Two-step Hydration Process of preparing non-fired bricks from the waste phosphogypsum (PG) is proposed.
- The use of cement is completely avoided and the PG content in the brick is as high as 75%.
- The 10 MPa press-formed brick has an excellent 7-day compressive strength of 29 MPa.

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ABSTRACT

Phosphogypsum (PG) is a solid waste mainly containing calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$). Preparing the non-fired wall bricks/blocks from PG is a prospective strategy for utilizing the waste. However, there are several shortages in the current technologies of PG brick production, such as, indispensable using of cement, high pressure in press-forming, high energy consumption in autoclaving–curing, and/or poor mechanical properties of bricks. This study proposes a novel "Two-step Hydration Process" for preparing PG non-fired bricks of a high 7-day compressive strength of 29 MPa, using no cement and a low pressure of 10 MPa in press-forming. The optimal formulation comprises 75.0% of PG, 23.47% of river sand and 1.53% of hydrated lime, and the water incorporation is 22% of all the above solids. The corresponding water absorption, weight loss and compressive strength after 15 freezing–thawing cycles of as-prepared 7-day bricks are 10.19%, 1.1% and 23 MPa, respectively, which fully meet the quality requirements of the highest MU25 grade in the Chinese standard (JC/T422-2007). This creative process has the potential to cost-effectively recycle the waste PG and solve its environmental pollution.

1. Introduction

Phosphogypsum (PG) is a waste by-product discharged from the production of phosphoric acid by the wet acid method [1,2]. It is composed primarily of calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$) and partially of some impurities, such as phosphate, fluorides, sulfate ions and organic matters [3–5]. In general, 4.5–5.5 tons of PG are generated for per ton of phosphoric acid production [6,7]. Currently, the worldwide PG generation is estimated to be around 100–280 million tons per year, and the average annual production of PG exceeds 22 million tons in China [8–11]. Such a great amount of PG not only occupies the land, but also results in environmental pollution [12]. Therefore, it is of great urgencies and interests to recycle this solid waste.

The PG waste is extensively used to replace the natural gypsum in view of their similarities in the aspects of the chemical composition and the binding feature. At present, PG is widely applied in such fields as agricultural fertilizers [13,14], soil stabilization amendments [15,16], cement retarder [17,18], cementitious binder [10] and building bricks/blocks [19,20]. Especially, much attention has been paid to the production of PG non-fired bricks/blocks [21–31].

A large number of studies on the preparation of PG non-fired bricks have been reported, and there are mainly two types of technologies: the autoclaving–curing process [21–26] and the high-pressure press-forming process [27–31]. In the former, the green bricks are press-formed at normal pressures (20–40 MPa) and then autoclaving–cured at the high temperatures of 100–180 °C for 4–8 h under the pressures of 0.8–1.2 MPa. In contrast, the latter process avoids the use of autoclaving–curing, however it employs a

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press-forming at a very high pressure of about 80 MPa. Thus, the two processes suffer from the shortages of high energy consumption and high production cost. Moreover, the as-prepared PG bricks are poor in mechanical properties (generally less than 15 MPa in the compressive strength). Meanwhile, the PG incorporation in the brick bodies is relatively low (generally no more than 30%), and thus the PG recycling efficiency is limited [32].

To promote the recycling of PG waste via the non-fired brick route, we have previously proposed an interesting process named as "*the Hydration–Recrystallization process*" [32], which produces a brick with the high PG incorporation of 75% coupled with an encouraging compressive strength of 21.8 MPa. Moreover, neither the energy-intensive autoclave–curing nor high-pressure press-forming was used in the process. A new cost-saving method of in-situ hydration–recrystallization of gypsum ($CaSO_4{\cdot}2H_2O$) press-formed at normal pressures and cured in natural condition was proposed and employed to provide the PG brick with an interlocking crystalline microstructure and the resulting favorable mechanical strength.

However, the above-mentioned Hydration–Recrystallization process is still imperfect. For example, the consumption of cement (4% in formulation) is indispensable, the press-forming pressure (30 MPa) is not low enough, and the compressive strength (21.8 MPa) is not outstanding. Therefore, further efforts are still demanded to optimize the process of preparing non-fired bricks from PG.

In this study, a newer and upgraded process named as "*Two-step Hydration Process*" was designed and systematically investigated. In the process, no cement was needed at all, the pressure in press-forming was reduced significantly to 10 MPa, and the compressive strength of PG non-fired bricks was improved to 29 MPa. The process details were depicted, the effects of the processing parameters on the properties of as-prepared PG non-fired bricks were studied, and the mechanism controlling the evolution of the PG bricks was analyzed.

2. Experimental

2.1. Raw materials

The phosphogypsum (PG) with the moisture content of 12.3% was obtained from a phosphoric acid factory in Jingmen city of Hubei province, PR China. Its chemical composition after dried in vacuum drying oven was measured by Chinese standard methods for chemical analysis of silicate rocks (GB/T14506-2010) [33] and the results are given in Table 1. The radioactivity of PG was measured by the Low Background γ-ray Spectrometer (GC4019) to be 2.34, 1.89 and 10.7 Bq/kg for Th-232, Ra-226 and K-40, respectively, which are far below the Chinese limits of radionuclides in building materials (GB6566-2010). In addition, the commercial hydrated lime with the $Ca(OH)_2$ content of 96.2% was used to neutralize residual acid in PG, and the dried river sand was applied as an aggregate.

2.2. Preparing the PG non-fired bricks

The flowchart of preparing non-fired bricks from PG by the Two-step Hydration Process is shown in Fig. 1. The detailed procedures are as follows: (1) Weighing PG (by dry weight) and dried hydrated lime at a weight ratio of 98:2, then mixing and aging for 24 h to neutralize the residual acid in PG [23,32]; (2) hot-drying the aged PG–lime mixture at 180 °C for 1 h to dehydrate dihydrate gypsum ($CaSO_4{\cdot}2H_2O$) into semi-hydrate ($CaSO_4{\cdot}0.5H_2O$); (3) weighing the PG–lime mixture, dried river sand and water, and then stirring homogeneously for 3 min; (4) press-forming the batch mixture into green bricks quickly; (5) naturally drying the green bricks for 1 day, to endow the bricks with certain early mechanical strength to sustain in the following procedures; (6) water-immersing the green bricks at room temperature for 0.5 h; (7) naturally curing the immersed bricks. Finally, PG non-fired brick samples were obtained, of which some bricks were prepared into solid shapes with the dimension of 115 mm × 115 mm × 53 mm to use as the specimens for property measurement, and the others were done into hollow shapes with the dimension of 240 mm × 115 mm × 53 mm only for exhibition.

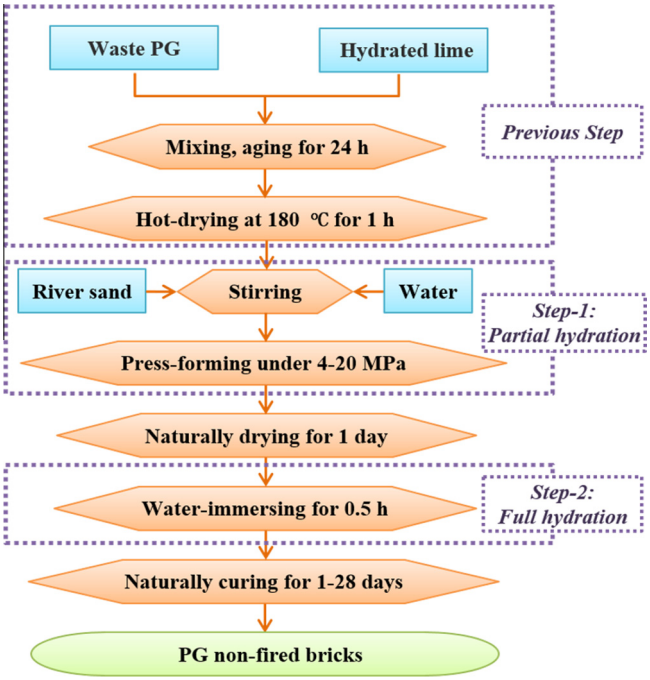

Fig. 1. Flowchart of preparing non-fired bricks from PG by the Two-step Hydration Process.

In order to investigate the effects of the processing parameters on the properties of PG bricks, the PG incorporation was adjusted within 65–85% with an interval of 5%, the water incorporation was varied from 14% to 30% with an interval of 2%, the press-forming pressure was varied from 4 to 20 MPa with an interval of 2 MPa, and the curing age was altered from 1 to 28 days.

2.3. Characterization

According to Chinese standard for wall bricks (GB/T2542-2003) [34] and for non-fired rubbish gangue brick (JC/T422-2007) [35], such properties as compressive strength, water absorption and freezing–thawing resistance of the PG non-fired brick specimens were respectively measured as follows: The compressive strength was measured at a loading rate of no more than 2 N mm^{-2} s^{-1}; The brick specimens were dried at room temperature in the vacuum drying oven, and then immersed in water at 20 ± 5 °C for 24 h, and then the weight change before and after immersing was calculated to characterize the water absorption; The compressive strength of some specimens after measuring water absorption were tested to evaluate the softening factor, which was calculated through dividing the value by the compressive strength of the dry specimens before water adsorption; Other specimens after measuring water absorption were frozen at −18 ± 1 °C for 5 h and thawed in water at 20 ± 5 °C for 3 h, and then the weight loss and compressive strength of the specimens after 15 freezing–thawing cycles were measured to characterize the freezing–thawing resistance. Five specimens for each performance were tested and the data were averaged. All the tests were conducted on the solid bricks.

The crystalline phase compositions of PG and the PG non-fired bricks were identified using X-ray Powder Diffractometer (XRD; D/Max-3B, Rigaku) with Cu Kα radiation, at 35 kV and 40 mA with 10 s scanning time. The microstructures of the specimens after coating with gold were observed by Scanning Electron Microscopy (SEM; SU8010, Hitachi) at 30 kV.

Table 1
Chemical composition of the waste PG dried in vacuum drying oven (wt.%).

Constituent	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	SO_3	Others	Ignition loss
Percentage	8.66	0.49	0.13	0.02	30.45	0.03	0.07	0.04	0.79	39.32	0.91	19.09