ARTICLE IN PRESS

Available online at www.sciencedirect.com

ScienceDirect

Ceramics International ▮ (▮▮▮▮) ▮▮▮–▮▮▮

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Preparation of hardened tiles from waste phosphogypsum by a new intermittent pressing hydration

Jun Zhou[a,b], Zimo Sheng[a], Tiantian Li[a,*], Zhu Shu[a,*], Yun Chen[a], Yanxin Wang[c]

[a]Faculty of Materials Science and Chemistry, China University of Geosciences, 430074 Wuhan, PR China
[b]Zhejiang Research Institute, China University of Geosciences, 311300 Hangzhou, PR China
[c]School of Environmental Studies, China University of Geosciences, 430074 Wuhan, PR China

Received 20 October 2015; received in revised form 18 January 2016; accepted 18 January 2016

Abstract

The solid waste phosphogypsum (PG), as the sole-raw material, was processed into hardened tiles with favorable mechanical strength by a novel intermittent pressing hydration process. First, the raw PG with dihydrate gypsum was dehydrated into semi-hydrate gypsum. The dehydrated PG was granulated with water, press-formed, and then immersed in water under intermittent pressing. Using the optimal granulation humidity of 35%, pressing pressure of 20 MPa, pressing frequency of once per 2 min and total times of 24, PG hardened tiles with bending strength of 18.9 MPa was obtained. It was revealed that the dehydrated PG was hydrated into the dense dihydrate gypsum crystals under the action of intermittent pressing, which contributed to the high mechanical strength of the tiles. The hardened tile has the potential to be a new-type wall material and its application may help to solve PG's environmental risk.

Keywords: Hardened tile; Phosphogypsum; Waste recycling

1. Introduction

Phosphogypsum (PG) is a solid waste by-product generated during the production of phosphoric acid from phosphate rocks [1–3]. The output of PG is estimated to be around 280 million tons per year all over the world. There are several approaches to utilize PG as resources. For example, in the sector of construction and building materials, PG can replace natural gypsum to produce gypsum board [4], non-fired brick [5,6], plaster [7], and especially the set retarder of Portland cement [8,9]. PG has also been used in the stabilized road bases in the civil engineering [10,11], and to modify the pH and calcium content of soil in agriculture [12]. Especially, in the chemical industry, PG is applied to producing sulfuric acid with joint production of cement [4]. There are also other PG recycling technologies such as building shoreline erosion structures [13] and using stabilized PG in the marine environment [14]. However, it is a pity that only about 15% [9] of PG is utilized and the remained majority has to be stored outdoors. This not only wastes the gypsum resources but also occupies a large amount of land resources and causes environmental problems. Hence, the massive and efficient utilization of PG is still of great importance and urgency.

Traditional building material such as ceramic tiles and gypsum plasterboards are widely used in architecture. China ranks first in the production of ceramic tiles all over the world, and has an output as high as 10.23 billion m^2 in 2014 according to *China Building Ceramics & Sanitaryware Association*. It is well known that ceramic tiles are generally manufactured by sintering to gain the excellent mechanical properties [15,16]. Nevertheless, the sintering procedure consumes massive fuels [17] and meanwhile discharges a great amount of exhaust gases. These energy consumption and environmental pollution issues have significantly limited the sustainable development of ceramic industry [18].

*Corresponding authors. Tel.: +86 18171239658; fax: +86 27 67883731.
E-mail addresses: taoshanzhe@126.com (T. Li), zhushu426@gmail.com (Z. Shu).

http://dx.doi.org/10.1016/j.ceramint.2016.01.117
0272-8842/

Please cite this article as: J. Zhou, et al., Preparation of hardened tiles from waste phosphogypsum by a new intermittent pressing hydration, Ceramics International (2016), http://dx.doi.org/10.1016/j.ceramint.2016.01.117

To solve the sintering-induced problems in ceramic manufacturing, some non-fired methods are proposed and developed. One alternative is using the organic/inorganic binders, such as phosphate cement [19–21] and unsaturated polymer resin. Nonetheless, the binders themselves are produced with high energy consumption and environmental pollution. Thus, it is neither environmental-friendly nor energy-efficient to use them. Apart from using binders, some other methods have also been developed recently to form strong bonds directly between the particles to prepare ceramic tiles without agglomeration, such as Mechano-chemical (MC) process [22–24] and alkali-activation [23]. For example, ceramic is prepared by the chemical solidification assisted with surface activation of the powder using the MC process. Nevertheless, these methods are unfavorable in view of their complex processes and may be not feasible in the industrial production.

In order to gain the non-fired ceramic tile via a simple method, we have previously proposed an interesting fabrication approach to process gypsum into non-fired tile by the continuous loading-hydration [25]. Neither energy-intensive nor complex procedure was used in the approach, and it produced a ceramic tile with an encouraging bending strength of 19.4 MPa. However, the approach is still imperfect. Especially, the hydration of tile need be carried out under continuous pressing, which is harmful for the permeation of water into the tile body and hinders the hydration reaction. Thus, a long-time processing (several hours) is needed, which significantly limits the industrial application.

In this study, an upgraded novel process of "*intermittent pressing hydration*" is designed by the authors to prepare hardened tiles from the waste PG. The mechanical performance of the hardened tiles is much superior to the gypsum plasterboards and comparable to the ceramic tiles, indicating its promising potential in wall materials. Substituting "intermittent pressing" (a minute-level procedure) in this process for "continuous pressing" (an hour-level procedure) in the previous pressing-hydration route makes it more feasible to realize the industrial manufacturing. In addition, it is worth emphasizing that PG is the sole raw material. Thus the massive and efficient recycling of the waste PG is also expected to be achieved by the process. This paper reports the design idea, process details and the major properties of the PG hardened tiles. The economic and environmental benefits of the process are also estimated preliminarily.

2. Experimental

2.1. Materials

PG was obtained from a phosphoric acid factory in Yichang city of Hubei province, P. R. China. The chemical composition of PG after being dried in vacuum drying oven was measured according to Chinese standard methods for chemical analysis of silicate rocks (GB/T14506-2010). The results are given in Table 1. The radioactivity of PG was measured by the Low Background c-ray Spectrometer (GC4019) to be 2.38, 1.81 and 10.2 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, since the main impurity is silica that is quite inert, its effect on the product is ignored in this work.

2.2. Specimen preparation

The process of *intermittent pressing hydration* for preparing the hardened tiles from PG are schematically shown in Fig. 1 and detailed as follows: (1) *Washing and dehydrating*. PG was washed to remove the residual acid until the leachate pH approached neutral, and then heated at 150 °C to dehydrate $CaSO_4 \cdot 2H_2O$ into semi-hydrate gypsum ($CaSO_4 \cdot 0.5H_2O$). (2) *Granulating and mold-filling*. 25 g of dehydrated PG was stirred with a certain amount of water to form granules. Then, the granules were immediately filled in a mold with the dimensions of 60 mm × 35 mm × 7 mm laid in a stainless steel tray. (3) *Hydrating under intermittent pressing*. The granules in the mold were preliminarily pressed into a compact under a destined pressure. Subsequently, water was poured into the tray till fully submerging the mold, and the compact in the mold was intermittently pressed at a destined frequency under the same pressure. (Noting: each pressing lasted for 2 s). (4) *Naturally drying*. After the intermittent pressing hydration, the formed tiles were de-molded and naturally dried for some days at room temperature to become the final products.

The water incorporation in the step (2) was varied from 15 wt% to 40 wt% with an interval of 5%. The loading pressure in the step (3) was varied from 5 to 35 MPa with an interval of 5 MPa. The frequency of intermittent pressing in the step (3) was varied from 4 to 32 times with an interval of 4 times and 2, 5 or 10 min for each pressing.

2.3. Characterization

The crystalline phase compositions of the dehydrated PG and the PG hardened tiles 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.

The bending strength of the specimens was measured by the bending test using a WAW1000D Microcomputer-controlled

Table 1
Themical compositions 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	Other	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

Please cite this article as: J. Zhou, et al., Preparation of hardened tiles from waste phosphogypsum by a new intermittent pressing hydration, Ceramics International (2016), http://dx.doi.org/10.1016/j.ceramint.2016.01.117