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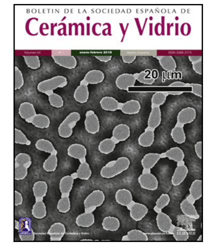

Calcium sulfate whisker reinforced non-fired ceramic tiles prepared from phosphogypsum

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ABSTRACT

Phosphogypsum (PG), an industrial by-product from the manufacture of phosphoric acid, can be processed into non-fired ceramic tiles by an intermittent pressing hydration process. In order to promote the practical application of the technology, calcium sulfate whisker (CSW) was used as reinforcing agent to increase the mechanical strength of PG tiles in this research. The bending strength of the resulted PG tiles with 1 wt.% CSW reached 27.2 MPa, a resulting increase of 80% compared to the specimen without CSW. The reinforcement of the mechanical strength is mainly attributed to the fact that, the dispersed CSW in the tile body act as "bridges" and strongly bond with gypsum crystals, thus forming a complete tighter-linked tile network.

Obtención de baldosas cerámicas crudas a partir de fosfoyesos reforzadas con fibras de sulfato cálcico

Palabras clave:
Sulfato cálcico en forma de fibras
Baldosas cerámicas crudas
Fosfoyesos

RESUMEN

Los fosfoyesos (PG), un residuo industrial obtenido en la fabricación de ácido fosfórico, pueden ser reutilizados en forma de baldosas cerámicas crudas, sin necesidad de una etapa de cocción, mediante un proceso intermitente de prensado e hidratación. Para poder llevar a cabo una aplicación práctica de esta tecnología, en este trabajo se propone utilizar sulfato cálcico en forma de fibras (CSW, por sus siglas en inglés) como agente de refuerzo, para incrementar la resistencia mecánica de las baldosas finalmente obtenidas. Con la adición de un 1% (en peso) de CSW se incrementó la resistencia mecánica a la flexión de las baldosas hasta un valor de 27,2 MPa, lo que representa una mejora del 80% con respecto a las baldosas de PG obtenidas sin adición de CSW. Este incremento en la resistencia mecánica a la flexión se atribuye a que el CSW actúa formando puentes que se enlazan fuertemente con los cristales de yeso, creando una red fuertemente unida.

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Introduction

Phosphogypsum (PG) is an industrial by-product resulting from the manufacture of phosphoric acid [1–3]. The main constituent of PG is $CaSO_4·2H_2O$, as well as some impurities such as fluoride, phosphate and organic matters. Currently, more than 22 Mt of PG [4] is generated per year in China. But only about 10% [5] is utilized via producing building materials such as PG bricks [6,7], plasters [8] and cement retarders [9,10]. The other 90% is still discarded without any treatment, which occupies a large amount of land and gives rise to environmental issues.

Ceramic tiles are widely used for wall and floor decoration in architecture. Generally, ceramics gain excellent mechanical properties by sintering [11,12], which not only consumes massive fuels [13] but also discharges lots of exhaust gases. Hence, some non-fired methods are proposed and developed. One alternative is using phosphogypsum to prepare non-fired ceramic tiles by an intermittent pressing hydration process [14]. The as-obtained ceramic tile has a bending strength of 18.9 MPa. Neither energy-intensive nor complex procedure was used in this process, meanwhile, PG was the only raw material, thus it is also an effective way to recycle waste PG. However, the mechanical properties of the tile is still imperfect for the industrial manufacturing.

In order to promote the practical application of the above-mentioned technology, we investigate the use of whiskers to further reinforce the bending strength of the PG non-fired ceramic tiles. Calcium sulfate whisker (CSW) is generally a kind of fiber-shaped single crystal. Due to its large length-to-diameter ratio, good toughness, high strength and cost-effectiveness [15,16], CSW is regarded as an attractive reinforcing agent in many fields such as papermaking [17], coating material [18] and paving asphalt [19]. Additionally, the main constituent of CSW is $CaSO_4·2H_2O$ and thus possesses an inherent compatibility with PG. Therefore CSW may act as an effective reinforcing agent for PG products.

Herein, CSW was investigated as reinforcing agent to improve the bending strength of the PG non-fired ceramic tiles, in view of its physical–chemical compatibility with PG. The CSW reinforced non-fired ceramic tiles show considerably enhanced bending strength of 27.2 MPa, being profitable for wide applications in practice. In this work, the optimal process parameters were determined, the effects of CSW on the mechanical strength, structure and morphology of non-fired tiles were investigated, and the strength evolution mechanism of the CSW/PG tiles was discussed.

Experimental

Raw materials

CSW (96% purity, 1–4 μm in diameter, 10–300 μm in length and a length-to-diameter ratio of 50–80) was obtained from Bokaili Ecological Engineering Co., Ltd., Zhengzhou, PR China. PG was supplied by a phosphate fertilizer factory in Dangyang city, Hubei province, PR China. After drying in vacuum oven, the chemical composition of the waste PG was measured according to Chinese standard methods for chemical analysis of silicate rocks (GB/T14506-2010). The results are given in Table 1.

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

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

Preparation of CSW/PG non-fired ceramic tiles

The CSW reinforced PG non-fired ceramics were prepared by the "intermittent pressing hydration" process and the detailed procedures are as follows:

(1) Washing PG to remove the residual acid and dehydrating it into semi-hydrate gypsum ($CaSO_4·0.5H_2O$) at 150 °C.

(2) Mixing 25 g of dehydrated PG with a certain amount of CSW (varied from 0 to 2.5 wt.% with an interval of 0.5 wt.%, basing on the mass of dehydrated PG) and a certain amount of water (varied from 15 to 40 wt.% with an interval of 5 wt.%, basing on the mass of dehydrated PG), granulating the mixture and immediately loading the as-prepared granules into a mold.

(3) Compacting the granules by destined pressure (varied from 5 to 35 MPa with an interval of 5 MPa). Subsequently, water was poured into the tray to fully submerge the mold, and the compact in the mold was intermittently pressed at a destined frequency of once per 2 min under the same pressure. The intermittent pressing times were varied from 4 to 28 with an interval of 4. Each pressing lasted for 2 s. In the course of intermittent pressing, semi-hydrate PG transformed into dihydrate PG.

(4) Drying the green bodies at room temperature and finally obtaining the non-fired ceramic samples.

Characterization

The bending strength of specimens was measured using a WAW1000D Microcomputer-controlled electro-hydraulic servo universal testing machine with a 40 mm span at a crosshead speed of 0.5 mm/min. The crystalline phase compositions of samples were identified using X-ray Powder Diffractometer (XRD; D/Max-3B, Rigaku) with CuKα radiation at 35 kV and 40 mA with 10 s scanning time. The microstructures of the whiskers and the ceramic specimens after coating with gold were observed by Scanning Electron Microscopy (SEM; SU8010, Hitachi) at 30 kV.