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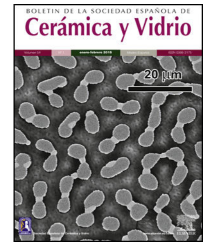

Calcium sulfate whisker reinforced non-fired ceramic tiles prepared from phosphogypsum

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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 $CaSO_4 \cdot 2H_2O$, 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 $CaSO_4 \cdot 2H_2O$ 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 ($CaSO_4 \cdot 0.5H_2O$) 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.

Results and discussion

Determination of optimal process parameters

Although CSW plays a decisive role on the bending strength of the as-prepared PG ceramic tiles, the process parameters in "intermittent pressing hydration" also have an influence on the tiles' properties. A series of experiments were carried out to determine the optimal process parameters.

The effect of water addition in the granulation step on the bending strength of tiles was investigated and the results are shown in Fig. 1. When the CSW content is 1 wt.%, the bending strength of the tiles rises from 18.5 to 27.2 MPa as the water addition increases from 15 to 30 wt.%, and then goes down rapidly to 20.6 MPa as the water addition goes up to 40 wt.%. It is believed that, with the aid of the surface tension and the lubrication effect of water, the loose dehydrated PG particles can be effectively granulated to improve the mold-filling density and further to avoid the delamination flaw of tiles in pressing. However, when excessive water (≥35 wt.%) is added, there will be excessive amount of semi-hydrate gypsum hydrated in the granulation step. The as-formed dihydrate gypsum crystals cannot be cross-linked with each other in the subsequent intermittent pressing hydration step, resulting in final PG ceramic tiles with decreased bending strength.

Fig. 2 illustrates the bending strength of tiles with different CSW contents pressed under converted loading pressure. The bending strength of PG non-fired ceramic tiles increases with the increase of pressure (≤20 MPa), and then maintains constant at further increased pressure (≥20 MPa). When the pressure increases to 20 MPa, the bending strength grows to a maximum value of 27.2 MPa. Such an increase trend of the mechanical strength of tiles can be attributed to the fact that, the high pressure helps eliminate air inside the green body to improve the compactness of the tile. Nevertheless, pressure above 20 MPa would not further increase the compactness, thus the optimal pressing pressure in the intermittent pressing hydration is 20 MPa.

The pressing times will affect the total hydration time and thus influence the degree of the hydration, and finally determine the bending strength of final non-fired tiles. The bending strength of the tiles with variable CSW incorporation as a function of pressing times is shown in Fig. 3. Obviously, with the increase of pressing times, the bending strength of tiles incorporated with different contents of CSW presents similar changing trend, that is, the bending strength increases first and then retains approximately unchanged. The reason lies in the fact that the total reaction time increases with the increase of the pressing times. Thus more semi-hydrate gypsum in the ceramic body can be transformed into dihydrate gypsum under the increased pressing time, which results in the improvement of bending strength.

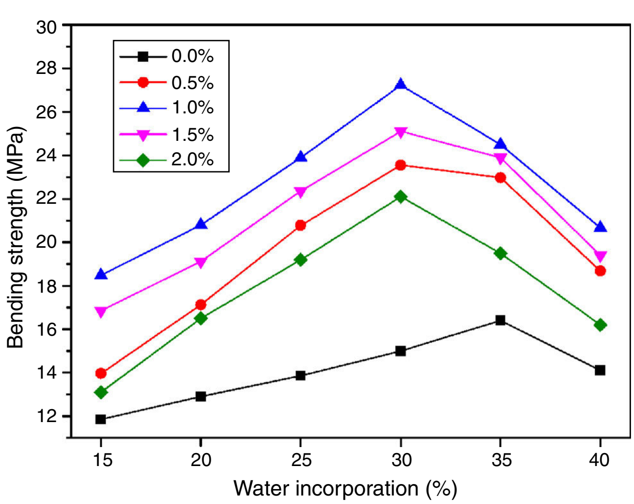

Fig. 1 – The bending strength of resultant phosphogypsum non-fired ceramic tiles versus the water addition in granulation. Other process parameters: pressure = 20 MPa, pressing times = 12.

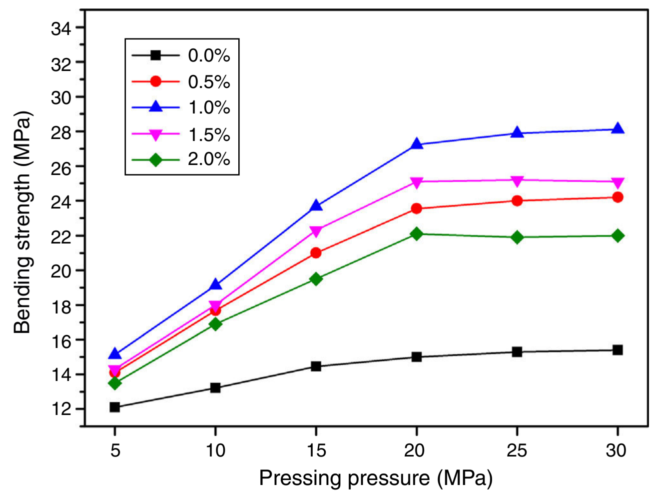

Fig. 2 – The bending strength of PG non-fired ceramic tiles versus the pressing pressure. Other process parameters: water incorporation = 30 wt.%, pressing times = 12.

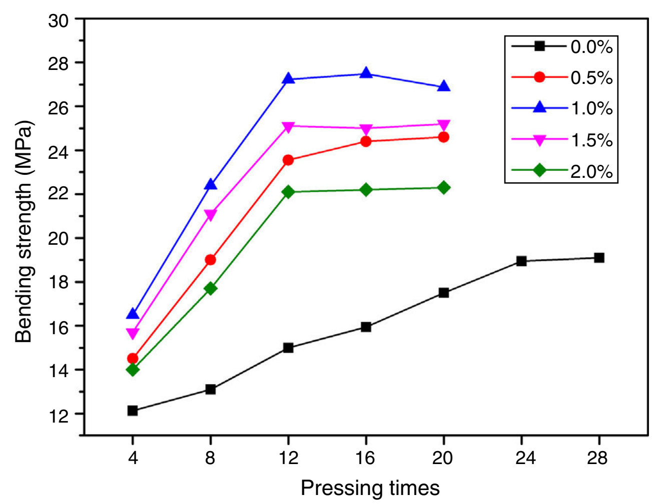

Fig. 3 – The bending strength of PG non-fired ceramic tiles with various pressing times. Other process parameters: water incorporation = 30 wt.%, pressure = 20 MPa.

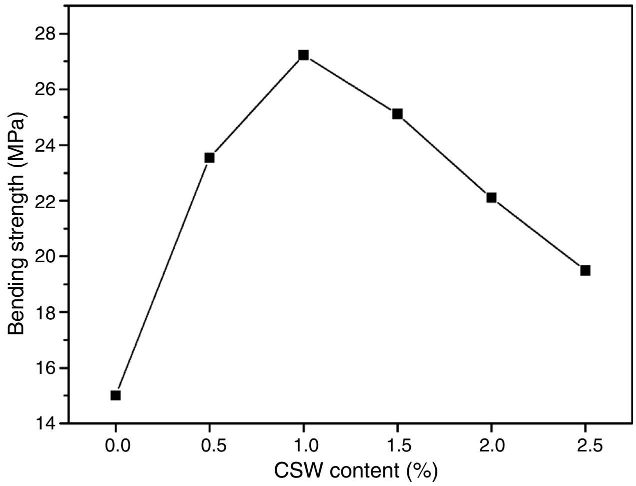

Fig. 4 – The bending strength of PG non-fired ceramic tiles versus the CSW contents. Other process parameters: water incorporation = 30 wt.%, pressure = 20 MPa, pressing times = 12.

Reinforcing effect of CSW on PG tiles

The data above (Figs. 1–3) preliminarily shows that CSW has a significant influence on the bending strength of the tiles. This section further details the effect of the CSW incorporation (0–2.5 wt.%) on the final PG non-fired ceramic tiles prepared with the optimal process parameters determined above.

As shown in Fig. 4, the bending strength of samples firstly rises from 15 to 27.2 MPa as the content of CSW increases from 0 to 1 wt.% and then decreased to 19.8 MPa at 2.5 wt.%. It is inferred that CSW integrates in situ with the dehydrated PG (semi-hydrate gypsum) and interlaces together during the granulation and press-forming. As the semi-hydrate gypsum hydrates into dihydrate gypsum during the intermittent pressing hydration, the high-strength CSW strongly bonds with the gypsum crystals and acts as "bridges" [20,21]. They finally form a compatible tighter-linked network within the whole tile. As a result, the PG non-fired ceramic tiles with higher bending strength can be obtained. However, whiskers with large length-to-diameter ratios are hard to be dispersed uniformly, and the connection of whiskers is much weaker than that between whiskers and gypsum crystals [22]. Therefore, the immoderate addition of CSW (1.5–2.5 wt.%) restrains the increase of bending strength.

The SEM observations of CSW and tiles processed with different CSW contents were recorded and shown in Fig. 5. CSW is high-regular fiber-like crystals with the aspect ratio ranging from 50 to 80 (Fig. 5a). It can be seen in Fig. 5b that the CSW-free PG non-fired tile is composed of columnar dihydrate gypsum ($CaSO_4 \cdot 2H_2O$) crystals, which stack together in an irregular arrangement with inter-crystal pores. When 1% CSW is incorporated in the tile (Fig. 5c), the whiskers act as a skeleton within the tile body. They strongly bond with the dihydrate gypsum crystals and bridge them together, resulting in the dense, highly crystalline structure of the as-prepared CSW/PG ceramic tiles. Benefiting from the whisker bridging enhancement mechanism [23], the CSW/PG ceramic tile has a

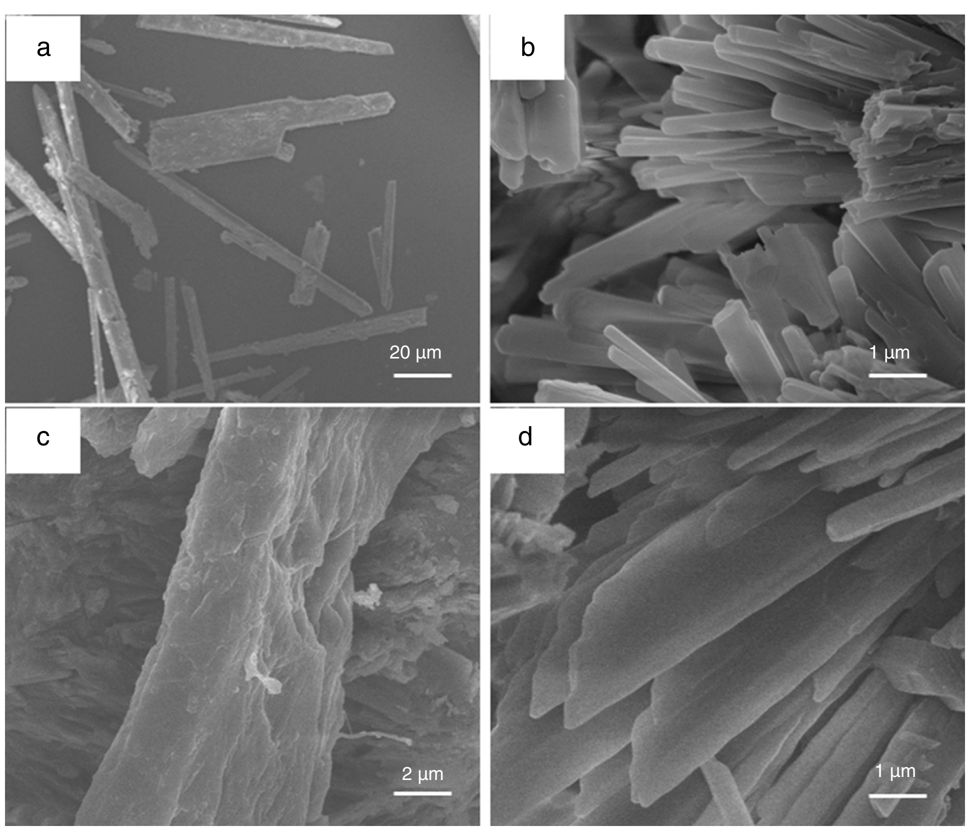

Fig. 5 – SEM images of (a) CSW and the non-fired ceramic tiles incorporated with (b) 0 wt.%, (c) 1 wt.%, (d) 2.5 wt.% CSW. Other process parameters: water incorporation = 30 wt.%, pressure = 20 MPa, pressing times = 12.

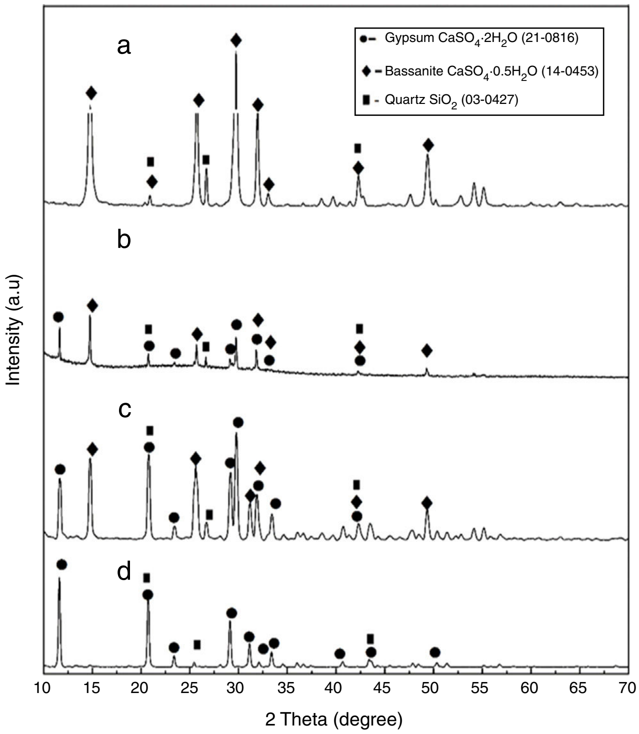

Fig. 6 – XRD patterns of (a) dehydrated phosphogypsum and the non-fired ceramic tiles pressed for (b) 4, (c) 8, (d) 12 times. Other process parameters: water incorporation = 30 wt.%, pressure = 20 MPa, CSW content = 1 wt.%.

significantly increased bending strength of 27.2 MPa in comparison with the CSW-free tile (15.1 MPa). However, further increasing the CSW content leads to a decrease in bending strength because whiskers with high aspect ratio are hard to uniformly disperse and agglomerate easily (Fig. 5d).

Effect of CSW on the strength development of PG tiles

To investigate the effect of CSW on the strength development of PG tiles, the XRD patterns of the tiles mixed with 1 wt.% CSW processed at 20 MPa for different pressing times were recorded and plotted in Fig. 6. It shows that, the hydration degree of tiles, i.e. the ratio of dihydrate gypsum to semi-hydrate gypsum, increases with the growing of pressing times, which is attributed to the correspondingly increased duration of hydration reaction. The hydration of the CSW reinforced non-fired ceramic tile completes after just 12 times of pressing, which decreases by half compared with the tiles without CSW (Fig. 3). The main constituent of PG is $CaSO_4 \cdot 2H_2O$ and has great compatibility with the CSW. It is believed that CSW can act as seed crystals for gypsum [24,25] and thus the dihydrate gypsum ($CaSO_4 \cdot 2H_2O$) crystals effectively grow along the CSW. Furthermore, in view of the whisker bridging mechanism, the porosity of the CSW/PG tile is slightly larger than that of the tile without CSW, so it is easier for water to penetrate into the CSW/PG tile body and further reduce the total hydration time of the tile. The decrease of the pressing times for the CSW/PG tiles and the increase of the final bending strength of as-prepared tiles are profitable for industrial manufacturing.

To sum up, for the preparation of the CSW/PG non-fired ceramic tiles, the optimal content of CSW is 1 wt.%, and the cost-effective and feasible technological parameters are 30 wt.% of water addition, 20 MPa of pressing pressure and 12 of pressing times. The tile prepared on the optimal conditions has the bending strength of 27.2 MPa, meeting the standard requirement (≥18 *MPa, Annex K (normative) Dry-pressed ceramic tiles (Group BIIb), ISO 13006:2012 Ceramic tiles – Definitions, classification, characteristics and marking*). Its photographs are shown in Fig. 7. The tile body looks like a “stone”

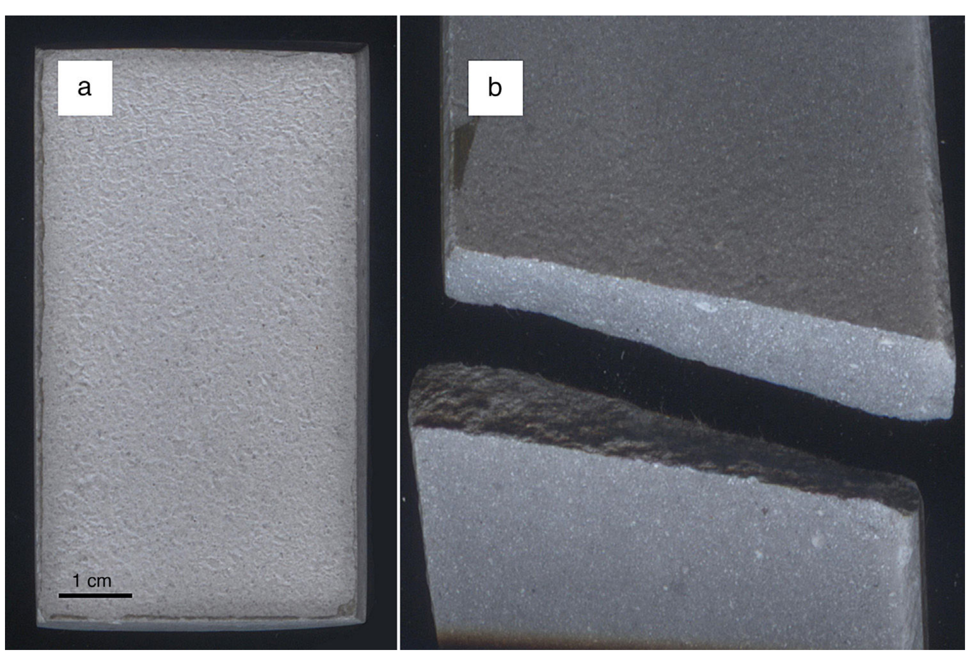

Fig. 7 – The photographs of (a) the surface and (b) the fracture section of the PG non-fired ceramic tile.

with a highly compact texture, and the appearance of its fracture section is similar to the commercially fired ceramic tile.

Conclusions

Calcium sulfate whisker (CSW) can be used to reinforce the phosphogypsum (PG) non-fired ceramic tiles. The optimum CSW content is 1 wt.%, and the corresponding as-prepared tiles have a high bending strength of 27.2 MPa, a resulting increase of 80% compared with the CSW-free tiles.

The reinforcement of the mechanical strength is mainly attributed to the fact that, CSW with high strength can strongly bond with gypsum crystals and act as "bridges", and thus form a tighter-linked network within the whole tile.

The addition of CSW can help improve the mechanical property of the product as well as reduce the total hydration time, which may extend its application and make it more feasible for industrial manufacturing.

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REFERENCES

[1] Y. Shen, J. Qian, Utilisation of phosphogypsum for sulfate-rich belite sulfoaluminate cement production, Adv. Cem. Res. (2015) 1–11.
[2] L. Yang, Y. Yan, Z. Hu, X. Xie, Utilization of phosphate fertilizer industry waste for belite–ferroaluminate cement production, Constr. Build. Mater. 38 (2013) 8–13.
[3] S.Q. Lu, P.Q. Lan, S.F. Wu, Preparation of nano-$CaCO_3$ from phosphogypsum by gas–liquid–solid reaction for CO_2 sorption, Ind. Eng. Chem. Res. 55 (2016) 10172–10177.
[4] J. Yang, W. Liu, L. Zhang, B. Xiao, Preparation of load-bearing building materials from autoclaved phosphogypsum, Constr. Build. Mater. 23 (2009) 687–693.
[5] Y. Huang, J. Qian, J. Liang, N. Liu, F. Li, Y. Shen, Characterization and calorimetric study of early-age hydration behaviors of synthetic ye'elimite doped with the impurities in phosphogypsum, J. Therm. Anal. Calorim. 123 (2015) 1545–1553.
[6] J. Zhou, D. Yu, Z. Shu, T. Li, Y. Chen, Y. Wang, A novel Two-step Hydration Process of preparing cement-free non-fired bricks from waste phosphogypsum, Constr. Build. Mater. 73 (2014) 222–228.
[7] J. Zhou, H. Gao, Z. Shu, Y. Wang, C. Yan, Utilization of waste phosphogypsum to prepare non-fired bricks by a novel hydration–recrystallization process, Constr. Build. Mater. 34 (2012) 114–119.
[8] M. Singh, Treating waste phosphogypsum for cement and plaster manufacture, Cem. Concr. Res. 32 (2002) 1033–1038.
[9] İ. Akın Altun, Y. Sert, Utilization of weathered phosphogypsum as set retarder in Portland cement, Cem. Concr. Res. 34 (2004) 677–680.
[10] Y. Erdogan, A. Demirbas, H. Genc, Partly-refined chemical by-product gypsums as cement additives, Cem. Concr. Res. 24 (1994) 601–604.
[11] J. Martín-Márquez, J.M. Rincón, M. Romero, Effect of firing temperature on sintering of porcelain stoneware tiles, Ceram. Int. 34 (8) (2008) 1867–1873.
[12] W.M. Carty, U. Senapati, Porcelain—raw materials, processing, phase evolution, and mechanical behavior, J, Am. Ceram. Soc. 81 (1) (1998) 3–20.
[13] A. Mezquita, J. Boix, E. Monfort, G. Mallol, Energy saving in ceramic tile kilns: cooling gas heat recovery, Appl. Therm. Eng. 65 (1–2) (2014) 102–110.
[14] J. Zhou, Z. Sheng, T. Li, Z. Shu, Y. Chen, Y. Wang, Preparation of hardened tiles from waste phosphogypsum by a new intermittent pressing hydration, Ceram. Int. 42 (2016) 7237–7245.
[15] Y.Q. Wang, Y.C. Li, A. Yuan, B. Yuan, X.R. Lei, Q. Ma, J. Han, J.X. Wang, J.Y. Chen, Preparation of calcium sulfate whiskers by carbide slag through hydrothermal method, Cryst. Res. Technol. 49 (2014) 800–807.
[16] W. Yuan, Y. Lu, S. Xu, Synthesis of a new titanate coupling agent for the modification of calcium sulfate whisker in poly(vinyl chloride) composite, Materials 9 (2016) 625.
[17] Q. Jiang, Y. Cheng, X.Y. Cao, R. Wei, M. Zhao, Preparation and physical properties of chitosan-coated calcium sulphate whiskers, Chem. Pap. 68 (2014) 1400–1407.
[18] H.C. Yang, T.P. Tasi, Enhanced soundproof performance of construction coatings using polyvinyl acetate resin and calcium sulfate whiskers, J. Mater. Civ. Eng. 28 (2016) 5.
[19] H.G. Zhang, P.W. Hao, X.S. Wang, Indoor research of high-modulus asphalt concrete with the added calcium sulfate whisker, in: X.J. Zhou (Ed.), Advances in Structural Engineering, Pts 1–3, Trans Tech Publications Ltd, Stafa-Zurich, 2011, pp. 90–94.
[20] C. Li, C. Bian, Y. Han, C.A. Wang, L. An, Mullite whisker reinforced porous anorthite ceramics with low thermal conductivity and high strength, J. Eur. Ceram. Soc. 36 (2016) 761–765.
[21] D. Sciti, L. Pienti, D.D. Fabbriche, S. Guicciardi, L. Silvestroni, Combined effect of SiC chopped fibers and SiC whiskers on the toughening of ZrB_2, Ceram. Int. 40 (2014) 4819–4826.
[22] Y.B. Wang, W. Zhang, C. Chen, T.S. He, Effect of curing time and $CaSO_4$ whisker content on properties of gypsum board, Appl. Mech. Mater. 507 (2014) 222–225.
[23] F. Han, Z. Zhong, F. Zhang, W. Xing, Y. Fan, Preparation and characterization of SiC whisker-reinforced SiC porous ceramics for hot gas filtration, Ind. Eng. Chem. Res. 54 (2015) 226–232.
[24] S. Halevy, E. Korin, J. Gilron, Kinetics of gypsum precipitation for designing interstage crystallizers for concentrate in high recovery reverse osmosis, Ind. Eng. Chem. Res. 52 (2013) 14647–14657.
[25] E.T. Tolonen, J. Ramo, U. Lassi, The effect of magnesium on partial sulphate removal from mine water as gypsum, J. Environ. Manage. 159 (2015) 143–146.