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Preparation of load-bearing building materials from autoclaved phosphogypsum

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Abstract

Previous studies have been carried out on calcined phosphogypsum (PG) for making the building materials. The present study was focused on autoclaved PG and its use in making load-bearing wall bricks. Autoclaved PG was prepared from original waste PG with steam pre-treatment. The crystalline phase, morphology, and thermal characteristics of original waste PG and autoclaved PG were investigated by XRD, SEM, and SDT. Then bricks of the size of Chinese standard brick were prepared from different types of PG in the PG-fly ash–lime–sand system. Results showed that the compressive strength of bricks from autoclaved PG by lower-pressure steam of 0.12 MPa, 120 °C for 16 h was much higher. The flexural strength and compressive strength of the bricks could reach 4.0 MPa and 15.0 MPa, respectively. The durability of the bricks was investigated by 15 freezing–thawing cycles at temperatures from −20 °C to 20 °C, and the weight loss was only 0.029% after all of cycles. Hemihydrates ($CaSO_4 \cdot 0.5H_2O$) were dehydrated products from dihydrates in original PG with lower-pressure steam treatment, and hemihydrates were susceptible to absorbing the humidity and were transformed into densified re-crystallization gypsum ($CaSO_4 \cdot 2H_2O$) that contributed to the final strength of bricks. Microstructural characteristics of bricks were investigated by XRD and SEM. Tobermorite was the significant hydrated product, which contributed to the strength of bricks. The use of autoclaved PG for making load-bearing wall bricks was recommended instead of conventional burnt clay bricks.

Keywords: Phosphogypsum; Building materials; Re-crystallization; Autoclaved; Solid wastes

1. Introduction

Waste phosphogypsum (PG) is an industrial by-product of phosphate production from phosphate ore or fluoroapatite. Over 6 million tons of PG is produced per annum in India and poses various environmental and storage problems [1]. The average annual production of PG in Turkey is about 3 million tons [2]. In Korea, 30 million tons of phosphogypsum is deposited as wastes [3]. The average annual production of PG is over 22 million tons in China, and the generation of PG is up to 280 million tons per annum throughout the world.

PG has been studied as set controller in the manufacture of Portland cement, as a secondary binder with lime and cement and in production of artificial aggregates and in road stabilization, as a raw material for wallboard and plaster after purified or calcined process [4–6]. However, currently only a small amount of PG is used in soil and road stabilization, and remaining are usually deposited in the open areas or dumped into river or sea. The lack of consumption possibility of PG causes landfill problem and environmental pollution [2].

On the other hand, building bricks industry is a huge consumer of the clay – conventional building material in China. Cultivated area of about 1.3 billion m^2 has been destroyed in the recent 50 years because of the production of burnt clay bricks. At the same time, the burnt clay bricks have consumed 70 million tons coal, with the emission of a huge amount of SO_2 and CO_2. For the amazingly increasing crisis of cultivated area, a new regulation was set up by Chinese government to forbid burnt clay bricks to be used as building

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materials in 170 major cities after 30 June, 2003. Therefore, enhanced constructional activities, shortage of conventional building materials and abundantly available industrial wastes have promoted the development of new building materials.

Efforts have been made to use PG in making building materials. The limited application of PG in building materials can in part be attributed to poor quality of building products directly made from unprocessed PG [7]. Calcined PG process has been mostly investigated as a pre-treatment process. However, there are two problems of current applications of calcined PG in building materials. Firstly, the content of calcined PG in building materials is lower than 30%, even less than 5%, only as an activation additive [2,3,8,9], which constricts the application of PG in large scale. In this paper, the unit of % means the percentage of weight. Secondly, the durability of building materials from calcined PG is unsatisfactory and is not competent for load-bearing building materials. In Chinese standards of unsintered building materials, such as autoclaved lime–sand brick (GB 11945-1999) [10] and fly ash brick (JC 239-2001) [11], the compressive strength and flexural strength of load-bearing wall bricks is higher than 15.0 MPa and 3.3 MPa, respectively. Moreover, compressive strength should be no less than 12.0 MPa, and weight loss should be no less than 2.0% after 15 freezing–thawing cycles at temperatures from −20 °C to 20 °C.

Previous studies have been focused on calcined PG and its use in the production of plaster boards [12–14]. However, current studies were seldom investigated on autoclaved PG and its use in the production of load-bearing wall bricks. In the present study, a pre-treatment process was carried out on waste PG with steam. Then autoclaved PG was applied in the production of autoclaved bricks as a major component in the PG-fly ash–lime–sand system. The strength and durability of bricks were tested, and the feasibility of bricks as load-bearing bricks was discussed.

2. Experiments

2.1. Raw materials

PG used in this study was obtained as a by-product during the production process of phosphoric acid in a phosphoric chemical factory in Xiangfan City of Hubei Province. Fly ash was obtained from the local coal-combustion power plant near the phosphoric chemical factory. Both lime and sand were obtained from the local construction materials market in Hubei Province. The composite additive was prepared by ourselves. The chemical compositions of raw materials are shown in Table 1.

Table 1
Chemical compositions of raw materials (%)

Constituent	Original PG	Fly ash	Lime	Sand
SiO_2	7.51	78.42	6.73	96.17
Al_2O_3	1.50	–	–	–
Fe_2O_3	0.15	2.86	–	1.99
CaO	32.10	1.85	60.11	1.34
MgO	0.43	1.65	1.50	–
SO_3	42.72	0.54	–	–
$K_2O + Na_2O$	0.12	–	–	–
P_2O_5	1.91	–	–	–
F	1.18	–	–	–
Loss on ignition	18.66	9.73	22.58	0.12

2.2. Pre-treating of waste PG with steam at different pressure conditions

In this research, a comparative study was conducted by using original waste PG and autoclaved PG as a main component in the production of autoclaved bricks.

Two types of autoclaved PG were prepared in the close container with steam at two different pressure conditions. The first autoclaved PG (called as LOW autoclaved PG) was prepared with lower-pressure steam at 0.12 MPa, 120 °C for 16 h, and second autoclaved PG (called as HIGH autoclaved PG) was prepared with higher-pressure steam at 0.8 MPa, 180 °C for 8 h.

Two different autoclaved PG samples from close container were immediately dipped in ethanol for 24 h in order to end hydration reaction. Then drying samples, compared with original waste PG, were investigated by XRD, SEM, SDT (Simultaneous DSC–TGA). SDT combines DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric Analysis). Powder X-ray diffraction investigations were carried out with D/Max-3B diffractometer using Cu Kα, operated at 40 kV and 40 mA and in the 2θ range from 3° to 65°. Morphology studies were carried out with JEOL 6340F FEGSEM scanning microscope after the samples coating with gold. SDT was investigated by TA instruments Q600 SDT, with air flow of 100 cm^3/min, from 20 °C to 1000 °C at the heating rate of 10 °C/min.

2.3. Preparation of brick specimens

The mix proportions of PG-fly ash–lime–sand bricks are given in Table 2. The designed experimental plan included three groups, noted as I, II, and III, respectively. Group I was designed to compare the effect of different types of PG. Group II was designed to study the effect of the content of PG; and group III was designed to study the effect of the content of lime. An important note of Table 2 is that LOW autoclaved PG was only used in experiments of both group II and group III because bricks made from LOW autoclaved PG exhibited much higher strength in the experiments of group I.

The mixtures were blended in a mechanical mixer uniformly. Suitable amount of water was added in the blending procedure. Steel mould of internal dimension 240 mm × 115 mm × 53 mm was used in order to keep the size of brick specimen the same as the size of standard burnt clay brick in China. Brick specimens were made by pressing in a hydraulic machine at a pressure of 20 MPa. The following curing process was carried out with a steam

Table 2
Proportions of PG bricks (%)

Mix designation	PG	Fly ash	Lime	Sand	Additive	Note
I-1	35	18	10	36	1	Original PG
I-2	35	18	10	36	1	LOW autoclaved PG
I-3	35	18	10	36	1	HIGH autoclaved PG
II-1	30	19	10	40	1	LOW autoclaved PG
II-2	40	16	10	33	1	
II-3	50	13	10	26	1	
III-1	40	18	5	36	1	LOW autoclaved PG
III-2	40	16	10	33	1	
III-3	40	15	15	29	1	

at the pressure of 0.80 MPa for 4 h in a local autoclaved fly ash brick plant. Autoclaved bricks were tested for compressive strength, flexural strength, and durability after staying in the air for over 24 h. All of test procedures were followed by Chinese test methods for wall bricks (GB/T 2542-2003) [15].

Broken brick specimen of III-3 after compressive strength test was immersed and saturated in ethanol for 24 h in order to end hydration reaction, then dried at 40 °C for 48 h. A small section of dried sample was prepared for morphology analysis after coating with gold for SEM analysis (JSM-5610LV); and the crystalline phase was investigated by powder XRD technique (D/Max-3B).

3. Results and discussion

3.1. Re-crystallization of PG in steam pre-treatment process

XRD patterns of different types of PG are shown in Fig. 1. Re-crystallization has taken place in steam pre-treatment process. In original waste PG, dihydrate ($CaSO_4 \cdot 2H_2O$) was the main crystal. In LOW autoclaved PG, hemihydrate ($CaSO_4 \cdot 0.5H_2O$) was the main crystal, with few un-modified dihydrates. In HIGH autoclaved PG, main crystal transformed from the dihydrate into anhydrite ($CaSO_4$) completely. Quartz phase (SiO_2) exited in all types of PG as a common inert impurity.

SEM images of three different types of PG are shown in Fig. 2. Original waste PG particles were irregular agglomerates, shown in Fig. 2a. However, autoclaved PG particles revealed the formation of euhedral prismatic and rhombic shaped crystals, shown in Fig. 2b and c. This indicated that re-crystallization generated in steam pre-treatment process, consistent with the XRD results.

SDT curves of three different PG are shown in Fig. 3. The weight loss of PG was observed in the range of 120–150 °C, which was due to dehydration reaction, accompanied by an endothermic peak in the DSC curves. During this dehydration stage, the weight loss of original PG was about 20%, which was higher than the weight loss of LOW autoclaved PG at about 10%. However, neither weight loss nor endothermic peak was observed in the SDT curves of HIGH autoclaved PG, which indicated that there was no dehydration reaction in the range of 120–150 °C. Stoichiometric calculations indicate that the weight percentage of H_2O in dihydrate, hemihydrate, and anhydrate is 20.93%, 6.21%, and 0%, respectively. Compared the weight loss in TGA curves with stoichiometric calculations of the weight percentage of H_2O, it was inferred that the main crystal of original waste PG was dihydrate, consistent with the XRD results in Fig. 1. Moreover, it was easily deduced that LOW autoclaved PG consisted of hemihydrate and few un-modified dihydrate, completely consistent with the XRD results in Fig. 1. The main crystal of HIGH autoclaved PG was anhydrite without dehydration reaction, also consistent with XRD pattern in Fig. 1.

3.2. Effect of different types of PG on the strength of bricks

The flexural strength and compressive strength of autoclaved bricks made from different types of PG are shown in

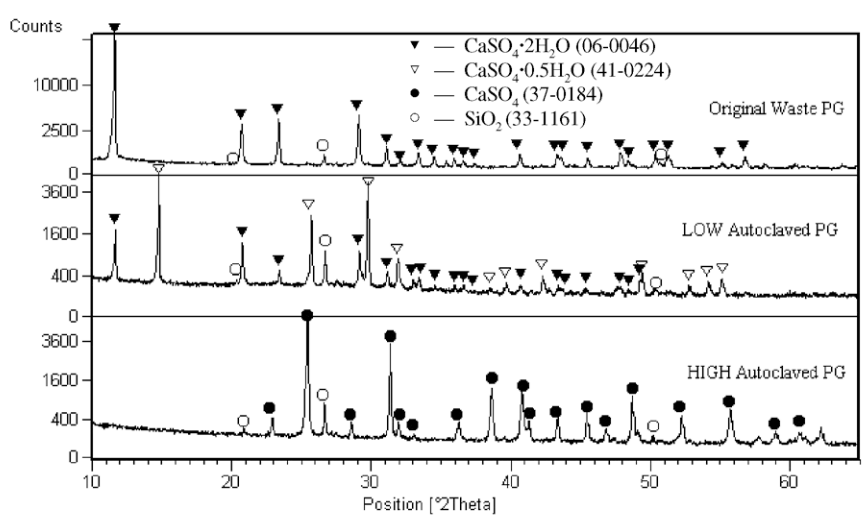

Fig. 1. XRD patterns of autoclaved PG compared to the original waste PG.

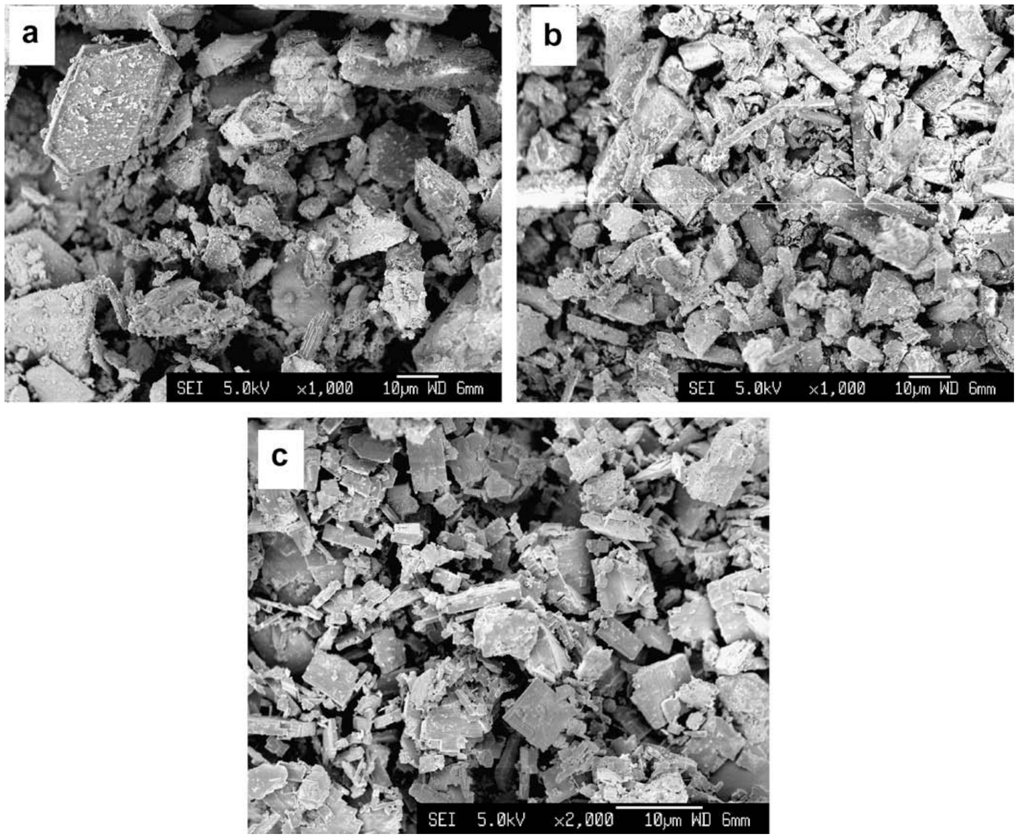

Fig. 2. SEM images of three different types of PG samples. (a) Original, (b) LOW autoclaved PG, (c) HIGH autoclaved PG.

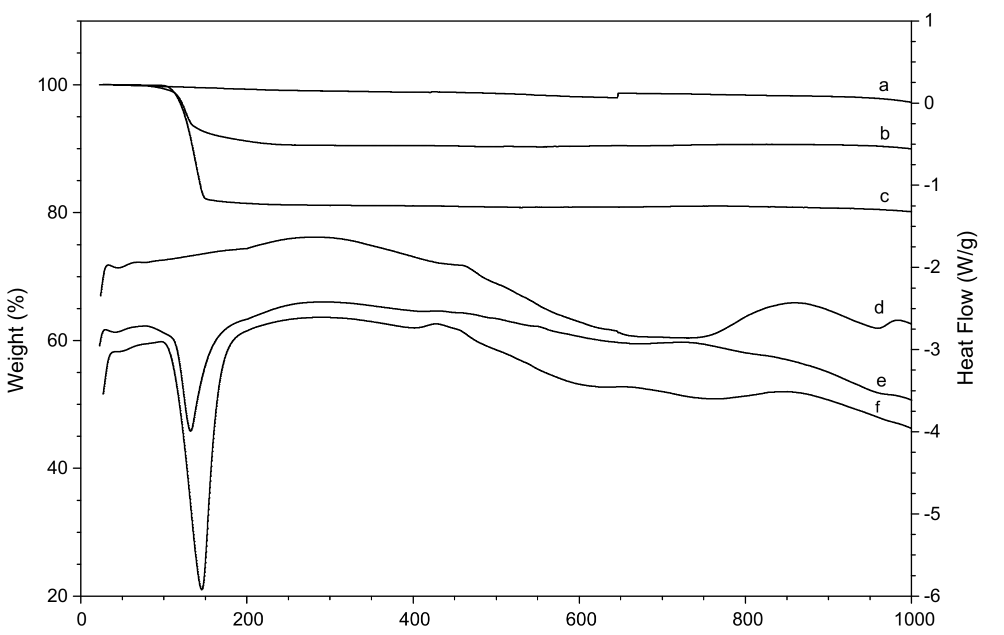

Fig. 3. SDT curves of three different types of PG. (a) TGA of HIGH autoclaved PG, (b) TGA of LOW autoclaved PG, (c) TGA of original PG, (d) DSC of HIGH autoclaved PG, (e) DSC of LOW autoclaved PG, (f) DCS of original PG.

Fig. 4. The strength of bricks from LOW autoclaved PG was the highest, and the strength of bricks from original PG was the lowest. This indicated that re-crystallization transformation of PG in steam pre-treatment process had significant effect on the strength of bricks. The hemihydrates generating under lower-pressure steam were suscep-

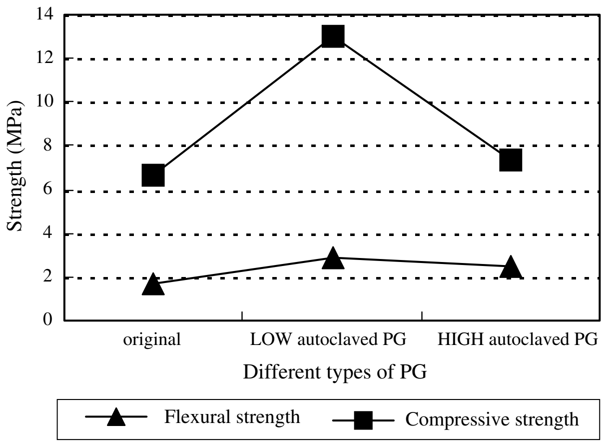

Fig. 4. Effect of different types of PG on the strength of bricks.

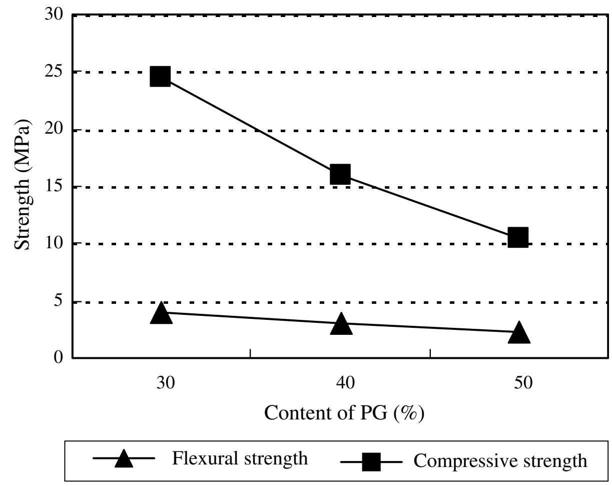

Fig. 5. Effect of the content of autoclaved PG on the strength of bricks.

tible to absorbing the humidity in the atmosphere, and were transformed into dihydrates again. The new-generating dihydrates appeared short column crystals, which led to densified net structure in the hydrated products. LOW autoclaved PG was only used in the following experiments because of its high strength.

3.3. Effects of the content of autoclaved PG on the strength of bricks

Effects of the content of autoclaved PG on the strength of bricks are shown in Fig. 5. The compressive strength decreased significantly with the increase in autoclaved PG content from 30% to 50%. If the content of autoclaved PG is more than 50%, it is difficult to reach the compressive strength of 10.0 MPa. At the content of 40% autoclaved PG, it is possible for the compressive strength to reach 15.0 MPa, which is the lower limit of the compressive strength of the excellent level in Chinese brick products.

With the increase of the content of autoclaved PG, it is hopefully benefit for effective consumption of PG, but negative impacts of PG as building materials on building environment should be paid attention to, such as the release of harmful vapors from PG. Extensive research is further needed. In the steam pre-treatment process, minor components such as fluoride, phosphate, and organic matter might be separated from autoclaved PG since they could be washed by the water in the dehydration reaction. This will also be investigated in further study.

3.4. Effects of the content of lime on the strength of bricks

Effects of lime content on the strength are shown in Fig. 6. With the increase of the content of lime, the compressive strength increased significantly, which indicated that lime played an important role in the PG-fly ash–lime–sand system. Lime not only acted as a necessary component of silica-calcium reaction, but also activated other hydrate reactions in PG-fly ash–lime system. Moreover, lime could eliminate the negative effect of acid and organic impurities on the strength to some extent.

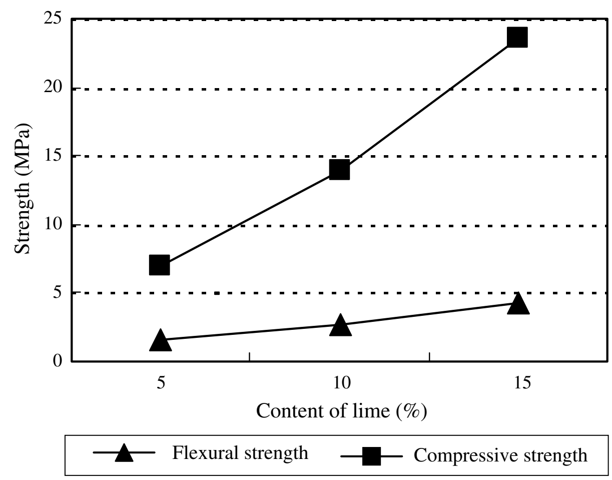

Fig. 6. Effect of the content of lime on the strength of bricks.

3.5. Strength mechanism of bricks from autoclaved PG

The XRD pattern of brick specimen III-3 is shown in Fig. 7. The major mineral phases were quartz (SiO_2) and anhydrite ($CaSO_4$), and comprising of some gypsum ($CaSO_4 \cdot 2H_2O$) and tobermorite ($5CaO \cdot 6SiO_2 \cdot 2H_2O$). Tobermorite, a kind of C–S–H with higher ratio of crystalline phase compared to C–S–H (I) gel, is the autoclaved product between SiO_2 in fly ash or sand and CaO in the lime at the steam of 0.80 MPa. The plausible mechanism of formation of tobermorite may be shown in Eq. (1). Tobermorite undoubtedly contributed to the strength of bricks because of its excellent mechanical properties. Some dihydrates in PG dehydrated into anhydrite, and some anhydrites and hemihydrates could transformed into gypsum ($CaSO_4 \cdot 2H_2O$) again in the PG-fly ash–lime–sand system. The re-generation of gypsum ($CaSO_4 \cdot 2H_2O$) might also contribute to the strength of bricks.

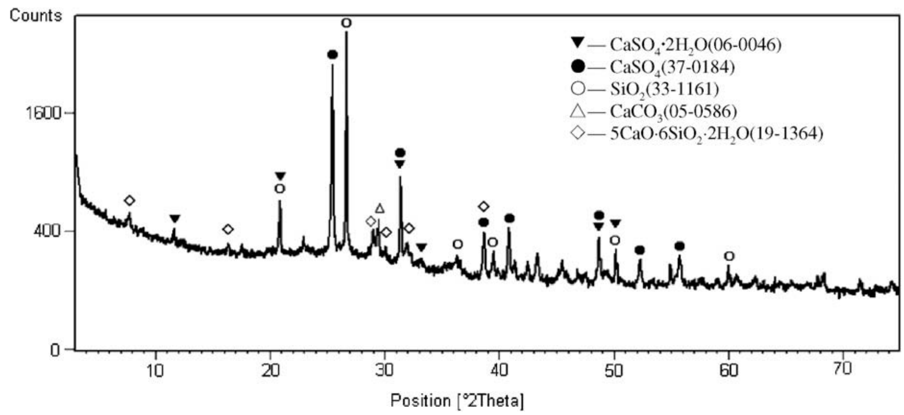

Fig. 7. XRD pattern of brick specimen III-3.

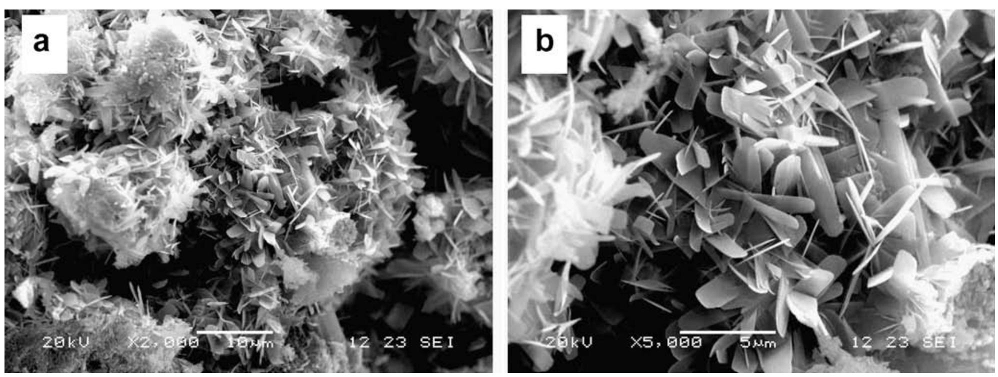

Fig. 8. SEM images of brick specimen III-3. (a) ×2,000, (b) ×5,000.

$$5CaO + 6SiO_2 + 2H_2O \overset{Steam}{\rightarrow} 5CaO \cdot 6SiO_2 \cdot 2H_2O \quad (1)$$

SEM images of brick specimen III-3 are shown in Fig. 8a and b. As shown, a large quantity of tobermorite with sheet-like shapes filled the interspaces of other particles, consistent with the XRD results in Fig. 7.

3.6. Durability of bricks made from autoclaved PG

The durability of brick specimen III-3 was investigated by 15 freezing–thawing cycles at temperatures from −20 °C to 20 °C, and the results are shown in Table 3. After all of 15 cycles at temperatures from −20 °C to 20 °C, the compressive strength of brick was 18.63 MPa, and the weight loss was only 0.029%, which indicated that the bricks owned good durability in humidity environment or cold climate. Compared with the Chinese wall brick standards (GB 11945-1999 and JC 239-2001), the bricks could be competent for load-bearing wall bricks.

Table 3
Results of freezing–thawing experiment of specimen III-3

Flexural strength before freezing–thawing cycles (MPa)	Compressive strength before freezing–thawing cycles (MPa)	Compressive strength after freezing–thawing cycles (MPa)	Weight loss after freezing–thawing cycles (%)
4.25	23.59	18.63	0.029

4. Conclusion

Dehydration and re-crystallization have taken place in original PG with the steam pre-treatment process. The crystalline phase has mostly transformed from dihydrate to hemihydrate ($CaSO_4 \cdot 0.5H_2O$) with lower-pressure steam of 0.12 MPa, 120 °C for 16 h; and the crystalline phase has completely transformed from the dihydrate to anhydrate ($CaSO_4$) with higher-pressure steam of 0.80 MPa, 180 °C for 8 h.

Bricks made from LOW autoclaved PG showed much higher strength, compared with bricks made from both original PG and HIGH autoclaved PG. It indicated that re-crystallization transformation of PG in the steam pre-treatment process had significant effect on the strength of bricks. Hemihydrates were dehydrated products with lower-pressure steam treatment, and hemihydrates were easily transformed into densified re-crystallization gypsum ($CaSO_4 \cdot 2H_2O$) that could contribute to the final strength of bricks.

From the results of microstructural characteristics of bricks by XRD and SEM, tobermorite was the significant hydrated product, which contributed to the strength of bricks because of its excellent mechanical properties.

Both strength and durability of bricks from LOW autoclaved PG showed that bricks could be used as load-bearing wall bricks instead of conventional burnt clay bricks.

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