

Gypsum blocks produced from TiO₂ production by-products

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ABSTRACT

Calcined titanium gypsum was investigated by the ways of XRD (powder X-ray diffraction), XRF (X-ray fluorescence) and TG-DTA (thermogravimetric–differential thermal analyses). It was employed as raw material for making lightweight materials. The influence of cement, amount of water/solid (W/S) ratio, water-reducing agent, citric acid content and the hydration age on the gypsum blocks was investigated. The results showed that the optimum W/S ratio, cement content and water-reducing agent are 0.9, 10% and 2 wt% for the calcined gypsum from titanium gypsum, respectively. The 5.96 MPa was attained after 7 days of ageing. It was also found that the citric acid is inappropriate to be used in the production of gypsum blocks from TiO₂ production by-products.

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1. Introduction

The use of waste materials and industrial by-products in the manufacture of Portland and blended cements, and ordinary and lightweight blocks undoubtedly contributes to the saving of natural resources and protection of environment.[1–10] Titanium gypsum is a by-product from the production of titanium dioxide (TiO₂) pigment. Because of the red colour imparted by the iron from ilmenite (FeTiO₃) ores, titanium gypsum is often called red gypsum.[11] Titanium is extracted from ilmenite by ways of concentrated sulphuric acid digestion; the excess acid (H₂SO₄) and iron sulphate (FeSO₄) are neutralized with lime or limestone, thus generating titanium gypsum, usually a by-product mainly composed of gypsum and iron hydroxide according to the following reactions [12]:



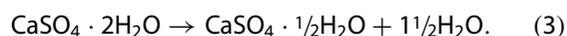
The slurry is separated by filtration from water which is partially recycled in the TiO₂ process. Titanium gypsum is usually landfilled or left or stacked nearby the titanium dioxide plant.

Similar to phosphogypsum,[13,14] flue gas desulphurization gypsum[15–17] and other solid wastes generated by sulphuric acid neutralization, titanium gypsum consists of calcium sulphate and impurities including fluorides, silica, organic matters and alkalis. The presence of impurities restricts the use of this by-product in building

materials field. Flue gas desulphurization of gypsum and phosphogypsum products is currently used in the cement and gypsum industries as set retarders for cement for making gypsum plaster and bricks.[18–25] Titanium gypsum is seldom used in the cement industry as a set retarder. There are few studies reporting its utilization for the production of gypsum bricks.

The waste disposal minimization could benefit both human health and environment in several industrial processes. In addition to the generation of the main product, the appropriate treatment of a fraction of the waste generated could obtain some co-products with economic value and broad application.[26,27] Obviously, the environmental and health impact of these co-products should comply with existing regulations at the national and international level.

The main potential utilization of titanium gypsum is to replace natural gypsum (CaSO₄·2H₂O) for making building materials. Calcined gypsum can be successfully produced from titanium gypsum by dehydration at 110–150°C. It is formed according to following equation (Equation (3)):



When the hydration reaction occurs, gypsum is formed again.[1] This compound is relatively soluble at 20°C, about 0.256 g in 100 g of water. Therefore, it cannot be utilized directly on the exterior of buildings because rain water could negatively affect its mechanical properties.[28,29]

Gypsum blocks are environmentally friendly and energy-saving materials due to their good properties, small dimensional change and easy application, and are very popular in buildings.[30,31] Natural gypsum has long been used as raw materials for gypsum blocks. The development of copper smelting processes resulted in a growing number of titanium gypsum-based waste stackings. The manufacture of gypsum blocks from titanium gypsum can consume great amounts of it. Not only can the stacking field of titanium gypsum in the copper smelting plant be reduced and secondary pollution avoided, but the exploitation of natural gypsum can also be decreased and the mining cost saved.

In this study, series of the gypsum blocks were prepared from calcined titanium gypsum. They were subjected to compressive strength and blending strength tests. The obtained results provide some positive suggestions as well as an effective way to recycle the neutral dregs and alleviate their impact on the environment and the economy.

2. Experiment

Titanium gypsum was supplied by the titanium dioxide plant Anhui Annada Titanium Industry Co., Ltd, in Tongling Anhui (south-eastern part of China). In order to obtain calcined gypsum, titanium gypsum was heated in an electric oven at 170°C for 2 h. Afterwards, it was stored in a desiccator at room temperature to avoid any contamination.

Commercial Portland cement (OPC), Zuanpai 32.5R (Hebei Yanxin Building Materials Co., Ltd.), naphthalene sulphonate-formaldehyde condensate (FDN), water-reducing agents (Muhu Concrete Admixture Co., Ltd) and Citric acid (Beijing Chemical Works) were used.

Powder X-ray diffraction (XRD) analysis was carried out using a Philips PW 1050 powder diffractometer (Cu-K α diffraction filtered by graphite and excited at intensity of 100 mA and tension of 40 kV), with the scanning rate 8°/min and the scanning range 5°–80° at room temperature.

The chemical composition of titanium gypsum was investigated by ways of X-ray fluorescence (XRF) analysis

(Thermo electron corporation) using Au ARL ADVANT XP + system equipped with Rh radiation operating at 50 kV.

Thermogravimetric–differential thermal analyses (TG–DTA) of the precursors were performed in air, from 20°C to 600°C, at a heating rate of 10°C/min.

Titanium gypsum and admixture samples were passed through a 4.75-mm sieve under dry conditions and mixed with regular tap water. They were cast into three-gang moulds and compacted by using a vibration table for 60 seconds. After demoulding, they were cured for 7 days at a relative humidity of 50% and 20°C. The apparent density of the materials was determined by measuring the weight and the dimensions of the produced materials. Porosity was evaluated according to Equation (4), where P' is the porosity (%), d_a is the apparent density and d is the bulk density measured by He pycnometer.

$$P'(\%) = \left(1 - \frac{d_a}{d}\right) \times 100. \quad (4)$$

The compressive strength of the gypsum blocks was determined according to Chinese standards (GB/T9776–2008: calcined gypsum) on samples 40 × 40 × 40 mm³. Mechanical tests were employed at a loading rate of 5 mm/min, and the results were the average of three specimens.

3. Results and discussions

The application of the calcined gypsum for building materials is limited by the presence of hemihydrate gypsum and impurities which have a great effect on the performance of the products. XRF and XRD analyses were carried out in order to determine the chemical and mineralogical components of titanium gypsum (Table 1 and Figure 1(a)). Table 1 shows that the chemical composition of titanium gypsum detected by XRF analysis. Titanium gypsum is mainly SO₃ (41.83%), followed by CaO (34.31%) and Fe₂O₃ (7.58%). As expected, CaSO₄·2H₂O is the main phase of titanium gypsum, as shown in Figure 1(a), and Figure 2 shows TG-DTA of titanium gypsum which loses weight at the range of 140–170°C as highlighted by two endothermic peaks. They were close to each other, so it is difficult to discriminate the point where one reaction ends and the other starts on

Table 1. Chemical composition of titanium gypsum test, mass%.

Compound	SO ₃	CaO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	TiO ₂	MgO
m/m (%)	41.830	34.310	7.580	2.910	2.250	1.230	0.842
Compound	Na ₂ O	MnO	V ₂ O ₅	Cl	K ₂ O	P ₂ O ₅	SrO
m/m (%)	0.434	0.251	0.081	0.060	0.053	0.044	0.032
Compound	ZnO	Cr ₂ O ₃	ZrO ₂	MoO ₃	Co ₃ O ₄	NiO	Others
m/m (%)	0.029	0.029	0.019	0.005	0.002	0.001	1.009

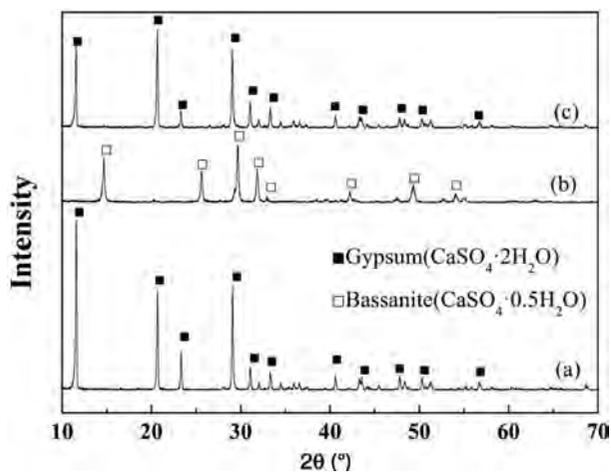


Figure 1. XRD patterns of (a) titanium gypsum; (b) calcined gypsum; (c) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in gypsum blocks.

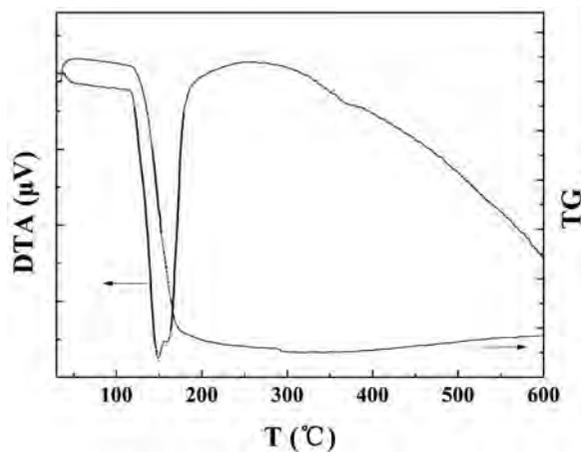


Figure 2. DTA-TG of titanium gypsum.

the TG curve. In the DTA curves, the main reaction is shown as translating to a hemihydrate compound. According to the TG curves, the first weight loss corresponds to the removal of $3/2$ water moles, and the second to that of $1/2$ water mole. Therefore, gypsum dihydrate transformed into β -calcined gypsum. The titanium gypsum was crushed and dried at 170°C . Because the titanium gypsum waste contains some impurities apart from titanium gypsum, the impurities are also involved in the reaction when being heated. The exact components of the impurities are unknown, and the amount of impurities is small in the waste. Therefore, we cannot explain the specific reasons for the increase at low temperature (temperature lower than 50°C) or the decrease at high temperature (temperature higher than 400°C) in weight. However, the presence of these impurities does not affect the use of titanium gypsum waste as raw materials to prepare gypsum blocks. From

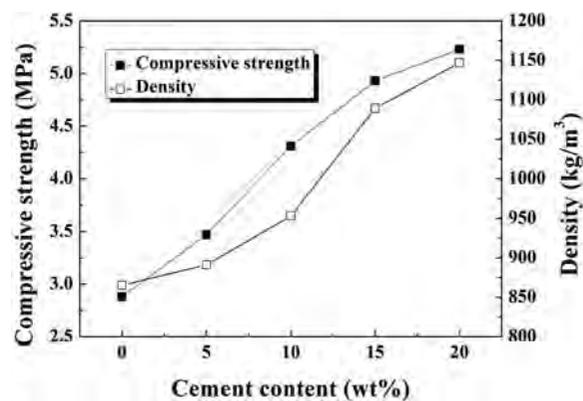
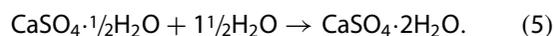


Figure 3. Influence of cement content on both compressive strength and density of gypsum blocks.

the XRD results (Figure 1(b)), after drying and dehydration, the main phases change to β -calcined gypsum and this calcined gypsum will be used after experiments.

Calcined gypsum firstly reacted with water to form gypsum dihydrate again (Equation (5)); at the same time, the crystal of gypsum grows fast in C-axis direction and easily into needle-like crystals. The intercross piling of the crystals enhanced the strength of the gypsum blocks. According to Equation (2), water demand for the hydration of gypsum is 19% by mass. However, this value is higher due to both water adsorbed by gypsum and that used for the mixing process.



As shown in Figure 3, when no cement was used, the compressive strength was 2.88 MPa. It was less than the minimum compressive strength values established by the Chinese National Standards, for the presence of impurities do not allow the gypsum blocks to reach the minimum compressive strength values. It is thus required to add certain amount of cement in order to improve the mechanical strength of gypsum blocks. The trend of compressive strength and density values with cement content is shown in Figure 3. By varying the amount of cement from 0% to 20%, the compression strength of gypsum blocks increased significantly (from 2.88 to 5.23 MPa). Also, the density values increased from 986 to 1237 kg/m^3 . As the Chinese National Standards required density value of a gypsum block is below 1000 kg/m^3 , cement content equal to 10% was established as the optimum additive amount; thus, compressive strength equal to 4.32 MPa and density value equal to 953 kg/m^3 were obtained.

The crystalline phases formed in the samples with different cement content are illustrated in Figure 4. It has been found that all the samples consisted of a dihydrate calcium sulphate characteristic peak. However, the

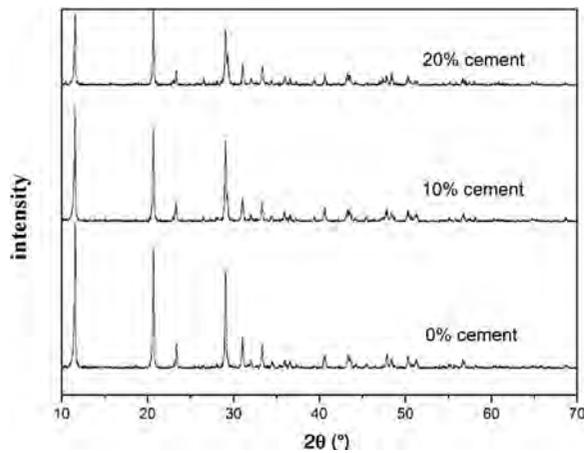


Figure 4. XRD patterns for gypsum block with different amounts of cement.

relative intensity gradually decreases with the increase in cement content, indicating the presence of more cement content in the samples. The cement pushed $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals to form a dense structure, hence increasing the compressive strength.

Moreover, water content has a great influence on the strength of gypsum blocks, and the water/solid (W/S) ratio is very important to study the preparation of gypsum blocks. The compressive strength and density of the gypsum element with the W/S ratio are shown in Figure 5. It can be observed that the density of the gypsum blocks decreases with the increase in the W/S ratio, but the compressive strength would descend with more water. This is mainly due to the formation of a porous structure resulting from water evaporation. The porosity of the samples is shown in Figure 6. These results show that an increase in the W/S ratio increased the porosity. The excess moisture will evaporate after moulding, thereby creating small holes; as a result the porosity of the samples increases. On

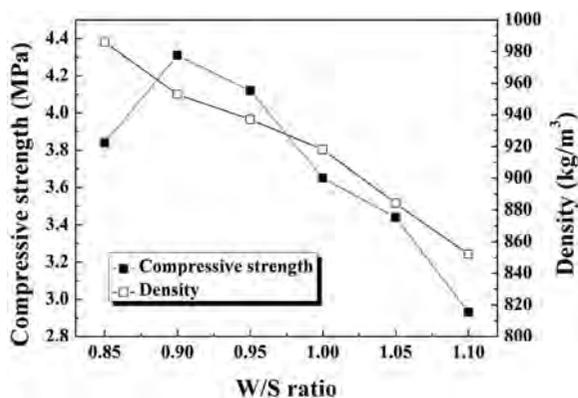


Figure 5. Influence W/S ratio on both compressive strength and density of gypsum blocks.

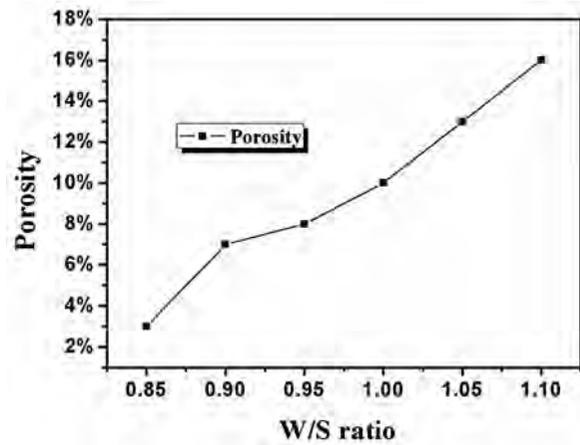


Figure 6. Influence W/S ratio on porosity of gypsum blocks.

the other hand, if the W/S ratio is too low, the raw materials exhibit higher viscosity value and hence reduced strength. Therefore, the best results in terms of compressive strength were obtained from a W/S ratio equal to 0.9.

The calcined titanium gypsum shows higher water absorption than calcined natural gypsum, thus requiring higher W/S ratio when gypsum blocks are prepared. This aspect showed compressive strength values which would decrease with more water. Thus, it is necessary to add a water-reducing agent in order to reduce the water demand and increase the compressive strength of gypsum blocks. FDN is a type of β -naphthalene sulphonic acid-based superplasticizer usually used as a water-reducing agent in gypsum, cement and other binding materials. The change in the W/S ratio and compressive strength with the FDN content is displayed in Figure 7. When FDN is added in amounts lower than 2 wt%, its effect is more evident and the density of the blocks significantly increased (from 953 to 1102 kg/m^3). When the FDN addition is higher than 9%, the effect is

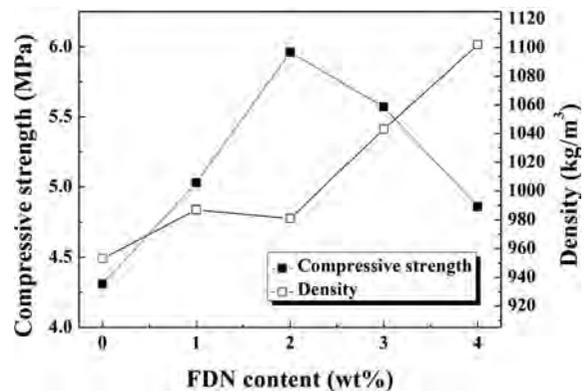


Figure 7. Influence of FDN content on compressive strength and density of gypsum blocks.

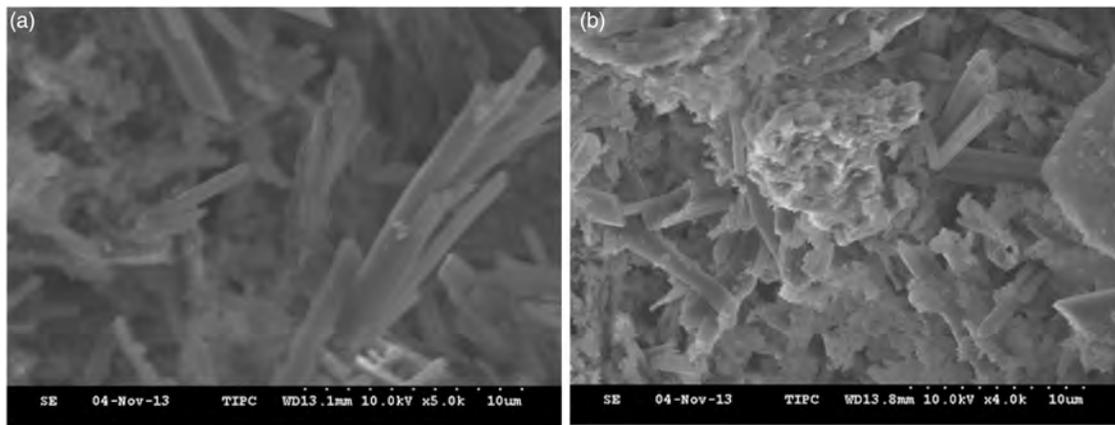


Figure 8. SEM image of (a) gypsum blocks without cement and FDN, (b) gypsum blocks containing 10% cement and 2% FDN.

not negligible, and the density change is also very small. Moreover, with the addition of FDN, the compressive strength of gypsum samples will increase. The highest compressive strength (5.96 MPa) is reached when the FDN content is equal to 2 wt% by mass. Further increase in FDN would reduce the compressive strength of gypsum blocks. So the optimum FDN content is 2 wt%, when the compressive strength value is equal to 5.96 MPa and the density is 981 kg/m^3 .

Figure 8 shows the SEM images for the gypsum block micro-structure from the sample without any admixture addition and the sample containing 10% cement and 2% FDN by mass. From the figures we can see that the semi-water gypsum transforms into crystals of dihydrous calcium sulphate through hydration reaction. A dense structure is formed as the crystals 'pack' together, which is the source of strength of the blocks. By comparing the two figures, we can see that in the former case, the structure is relatively loose, while in the latter case, the cement and FDN formed gelatinous and rod-like materials. These materials formed besides dihydrous calcium sulphate in the hydration process and they

intersect and overlap each other, thus increasing the compressive strength.

Sometimes it is necessary to add a retarder in the process of preparing gypsum blocks to prolong the solidification time of calcined gypsum and make the process easier. Citric acid is a common retarder for gypsum. The effects of the citric acid content on the compressive strength and density of the gypsum blocks are illustrated in Figure 9. The results indicated that even the addition of a small amount of citric acid will have a significant impact on the compressive strength of gypsum blocks. When 0.5% by mass of citric acid is added, the compressive strength of gypsum elements is only 0.51 MPa. Citric acid can be a proper retarder if only hemihydrate was used to prepare gypsum blocks. The experiment results showed that citric acid is inappropriate to be used to prepare gypsum blocks by using TiO_2 production by-products. Maybe it is the impurities in the by-products that have an influence on the use of the retarder. We did not also find another alternative as a retarder to

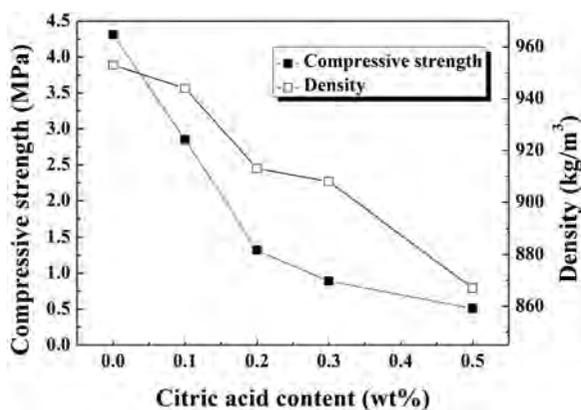


Figure 9. Influence of citric acid content on compressive strength and density of gypsum blocks.

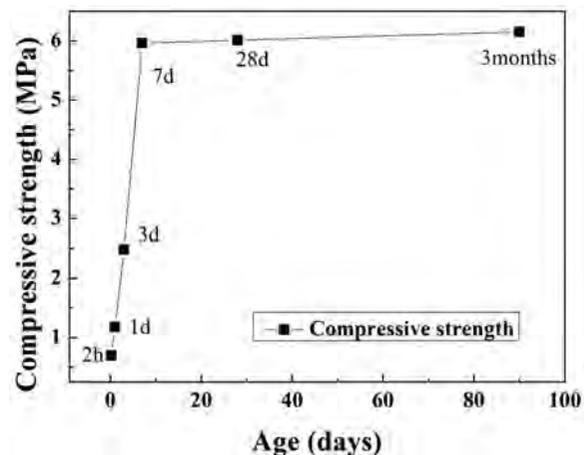


Figure 10. Compressive strength values of gypsum blocks with curing periods.

improve the mechanical properties of the prepared samples. The experiment of adding a retarder demonstrated that it is unnecessary to use a retarder for the preparation of titanium gypsum when using TiO_2 production by-products.

Compressive strength measured in the previous experiments was the strength after 7 days of forming blocks. But the strength of gypsum blocks will develop in the hydration process of calcined gypsum. Compressive strength of gypsum blocks at different ages of curing is depicted in Figure 10. The results show that the compressive strength at 2 h and 1 day is very low (only 0.7 MPa and 1.18 MPa, respectively). After 3 days of curing, the compressive strength rises to 2.48 MPa, and while at 7 days it rises up to 5.96 MPa. After 7 days, the increase of compressive strength is almost negligible.

4. Conclusion

Gypsum blocks, lightweight gypsum-based building materials, in this study were prepared by using calcined gypsum from Neutralization Sludge of Copper Smelting. The influence of cement amount, W/S ratio, water-reducing agent, citric acid content and hydration age on the gypsum blocks was evaluated. The results showed that the best W/S ratio, cement content and water-reducing agent are 0.9, 10% and 2 wt%, respectively. The maximum compressive strength of gypsum blocks was 5.96 MPa after 7 days of curing. It has also been found that citric acid is inappropriate to be used for the production of gypsum blocks. The outcomes of our experiments are positive, suggesting an effective way to recycle neutral dregs and find extensive applications in manufacturing building components and materials. The utilization of titanium gypsum in the construction materials industry could not only provide a low-cost material, but also contribute to lessening the environmental impact.

Disclosure statement

No potential conflict of interest was reported by the authors.

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