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SHORT RESEARCH AND DISCUSSION ARTICLE

An effective treatment method for phosphogypsum

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Abstract

Phosphogypsum (PG) accumulation occupies huge amounts of land resources and results in serious environmental risks. A new recycling product, the phosphogypsum embedded filler (PGEF) made with calcination-modified phosphogypsum, was developed. The preparation process, hydration mechanism of PG, basic physical performances, environmental safety, engineering application, and cost analysis of the PGEF were studied. The results showed that the stress performance and thermal insulation property of the products were satisfied. Environmental performance tests established their findings that the application of PGEF prepared with calcination-modified PG does not cause any secondary contamination. In addition, the cost of PGEF is far lesser than that of the same volume of reinforced concrete. PGEF prepared with calcination-modified PG has shown a perfect application in cast-in situ concrete hollow floor structure.

Key words Phosphogypsum · Large-scale · Utilization · Environmental

Introduction

The resource utilization of phosphogypsum (PG) has been studied by numerous papers, and the results of those studies show that PG can be used as raw materials for the preparation of finer aggregates supplementary cementitious materials, or the mine backfill, cement, mortar, bricks, and whisker (Chen et al. 2017; Wang et al. 2009; Li et al. 2008; Shen et al. 2012, 2014; Taher 2007; Huang et al. 2016; Nigade and Bagade 2015; Yang et al. 2016; Mun et al. 2007; Türkel and Aksin 2016; Garg et al. 2011; Zhou et al. 2014; Ma et al. 2018; Sheng et al. 2018). However, most of those researches focus on the resource utilization of PG in a laboratory scale, because of the high production cost, long-term durability, and environmental risks of the products prepared with PG.

In this case, a novel building material, the phosphogypsum embedded filler (PGEF) used in cast-in situ concrete hollow floor structure, was developed using modified phosphogypsum. The application of PGEF in floor structures possesses the advantage of steel, concrete saving, and building weight reduction. In addition, because of the PGEF used in floor structure was wrapped and protected by concrete, the long-term durability of the PGEF in structures also can be ensured effectively. What's more, the preparation of PGEF could consume a great number of PG, because of above 60% of the total mass of the raw materials of PGEF is calcination-modified PG (the rest are mainly water).

Therefore, the engineering application of PGEF has many environmental and economic benefits to be popularized. In this study, the physical properties, microstructures, and environmental performances of PGEF were investigated. In the meantime, modern analytical procedures were used to study the early hydration process and hydration products of PGEF. This study offers an alternative technique to the safe utilization of phosphogypsum. Furthermore, the cost of production of PGEF is much lower than that of same volume-reinforced concrete, exhibiting an excellent application foreground of PGEF (Fig. 1).

Materials and methods

Modified phosphogypsum was obtained from phosphate fertilizer plant in Chongqing, China. Polypropylene fiber is

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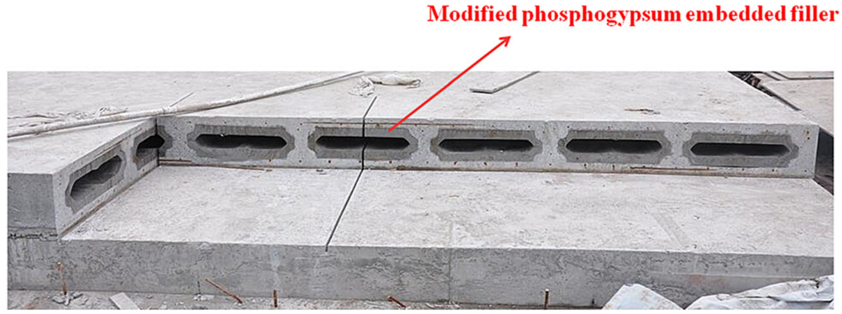
Fig. 1 PGEF used in floor structure



sourced from a local company. Coagulant was the analytical pure Na_2SO_4.

Mixing proportions and test methods

Mixing proportions and preparation of the PGEF

Based on the results of preliminary experiments, the mixing proportion (mass ratio) of PGEF is followed as 60% modified phosphogypsum, 0.5% polypropylene fiber, 0.5% coagulant, and 39% water. The modified phosphogypsum, polypropylene fiber, and coagulant were mixed uniformly with a mixer for about 0.5 min, and then the mixture was slowly mixed for about 2 min at a speed of 50 rpm once the water was added. The size of PGEF specimens was 580 mm × 580 mm × 100 mm, and then the specimens were demold and moved into storage yard for curing under natural condition.

Test methods

The crystalline minerals and hydrated products of the PGEF were identified using XRD (X-ray powder diffraction), conducting in a PANalytical (X'Pert PRO diffractometer) with an accelerating current of 60 mA and the voltage of 35 kv. The obtained spectrum was analyzed using software Plus MDI Jade 5.0.and X'Pert High Score, and the morphology of hydration product was investigated by a scanning electron microscope (ASTEREO SCAN440, Leica Cambridge Ltd). In addition, the chemical groups and bonds contained in hydration products of the PGEF samples were characterized by Fourier transform infrared (FT-IR).

Leaching property

According to the requirements and testing methods of standard, the environmental performance of the PGEF was determined.

Results and discussion

Linear equation and failure mode

The regular isosceles tetrahedron shaped was the embedded filler, wider at the curved design of decomposition of the stress, and the graceful arc formed by the arch. So the stress condition is similar to circular arc. Uses vertical uniform load, based on the standard basic solution of ordinary differential equation, formulas for computing stresses of embedded filler under vertical axial force are derived. So the arch axis diagram and equation was as shown in Fig. 2 and the equation is as follows:

$$y = Y \times 4\mathrm{x}^2/\mathrm{L}$$

When the load F becomes smaller, the PGEF can maintain the static equilibrium. As the load increases, the stress line was redistributed, and departs from axis increases. As shown in the Fig. 3(b), the cracks appears in spot E, and as the load increases, the cracks appears in spots G and H, leading to the breakage of PGEF. All in all, the stress performance of PGEF was satisfied.

Figure 4 shows a mathematical model of natural convection in PGEF. In order to maintain stability of fluid in the embedded filler, this will not appear as heat convection, so we can calculate the optimum air layer thickness. The calculation formulas of convection critical index Ra and Grashof number Gr were shown below:

$$\mathrm{Ra} = \mathrm{Gr} \times \mathrm{Pr}$$

$$\mathrm{Gr} = \mathrm{g}\beta\Delta\mathrm{TH}^3/\mathrm{v}^2$$

The Fourier law of heat conduction analysis method is used for planomural, and through the heat flow equals of the all cross section. So the calculation formula of heat flow was shown below.

$$q = \mathrm{ka} \times A \times \Delta\mathrm{Ta}/\mathrm{Ha} = \mathrm{kb} \times A \times \Delta\mathrm{Tb}/\mathrm{Hb}$$

It can be obtained by formula calculation that the optimum air layer thickness is 0.02 m. At this point, the thermal insulation property of modified phosphogypsum embedded filler was very well.

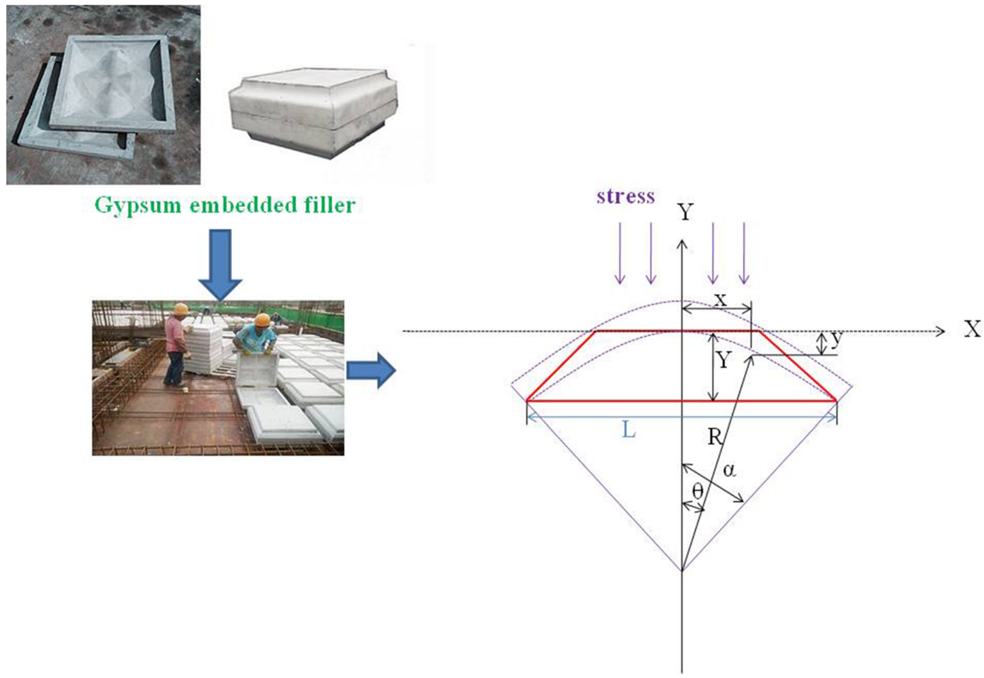


Fig. 2 PGEF's linear equation

Microstructure analysis

Figure 5 shows that the main mineral phase of the original phosphogypsum was $CaSO_4 \cdot 2H_2O$. However, the mineral phase of and the PGEF was $CaSO4 \cdot 2H_2O$, and the characteristic peaks at 2θ = 12°, 20°, and 30° were greatly increased, indicating that the preferred orientation growth constantly of $CaSO_4 \cdot 2H_2O$ as calcination temperature and time increases (Zhang et al. 2007). According to the SEM graph, it can be observed that the $CaSO_4 \cdot 2H_2O$ formed in PGEF presented a dense, regular, and interlock microstructure (Nurhayat Değirmenci 2008; Taher 2007; Vimmrová et al. 2014). In addition, the infrared spectrum of the original phosphogypsum and the hydration products formed in PGEF was shown in Fig. 5. The outcomes indicate that the infrared absorption peak at 1124.0 cm^{-1} corresponds to symmetric and asymmetric stretching vibrations ofSO_4^{2-} (sulfate radical). The 3437.8 cm^{-1} absorption peak corresponds to the stretching vibration and bending vibration of H–O. The intensity of absorption

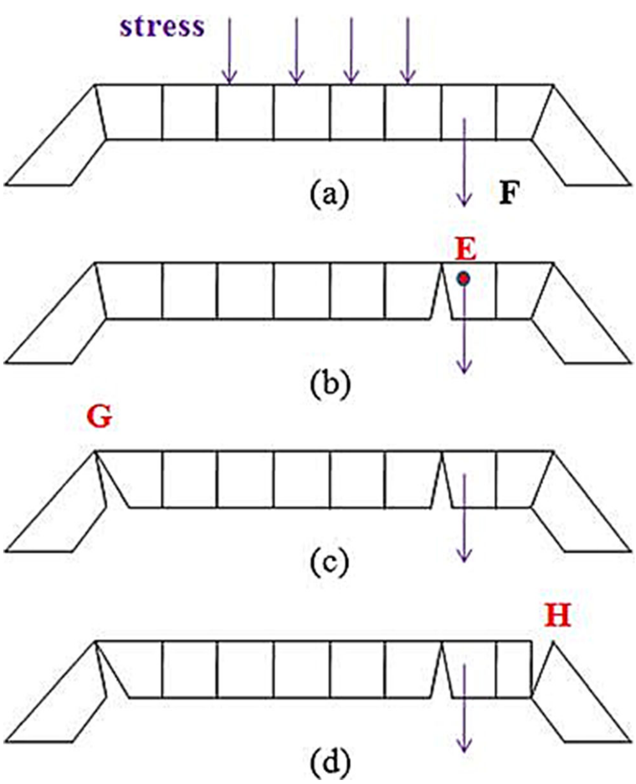


Fig. 3 PGEF's failure mode

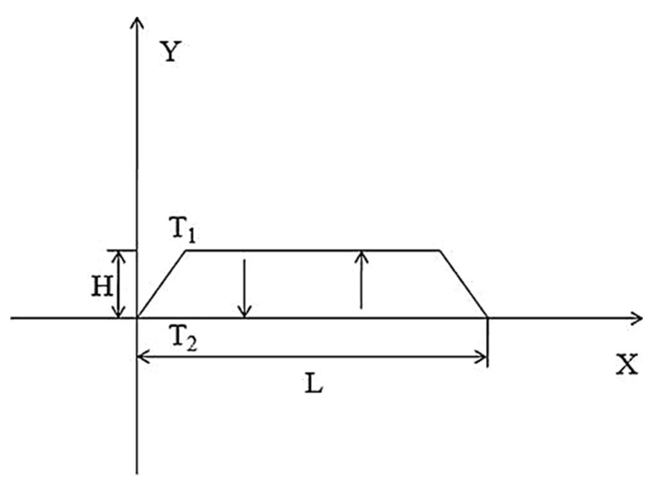


Fig. 4 PGEF's mathematical model of natural convection

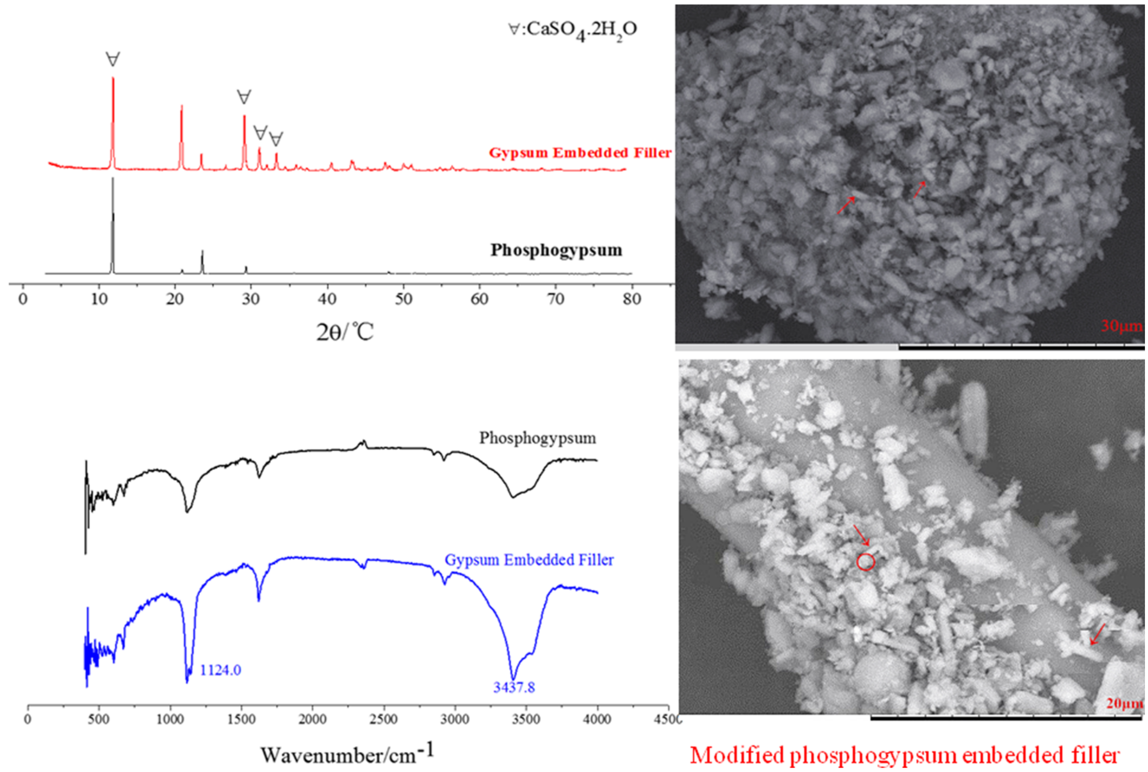


Fig. 5 Mineral phases of the phosphogypsum and embedded filler

peaks assigned to sulfate radical and hydroxide radical of PGEF is significantly increased compared with that of phosphogypsum. It also directly proven the possessing of hydration reaction of the hemihydrated gypsum with H_2O and hydration–recrystallization action with definite strength (Radwan and Heikal 2005; Wang et al. 2019).

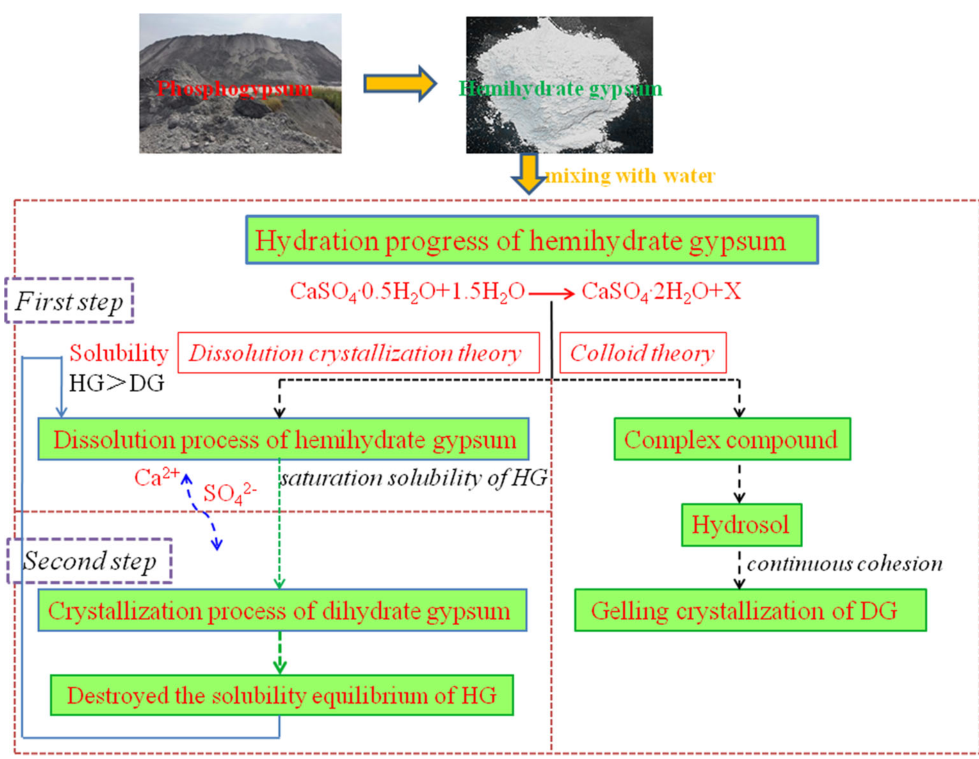


Fig. 6 Hydration progress of hemihydrated gypsum. Notes: HG is hemihydrated gypsum, DG is dihydrategypsum

Table 1 Lixivium content of heavy metal pollutants (unit: mg/L)

Item	Cu	Zn	Cd	Ni	As	Cr	Hg	Pb	Ba	P
Standard value	0.5	2.0	0.1	1.0	0.5	1.5	0.05	1.0	—	0.50
Detection value	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.81	0.46

N.D. is undetected

In short, the regular, dense, and interlock crystalline microstructure of the $CaSO_4 \cdot 2H_2O$ formed by recrystallization of hemihydrated gypsum ($CaSO_4 \cdot 0.5H_2O$) in situ promotes the development of mechanical properties of PGEF (Fig. 6).

Environmental safety analysis

It is clear from Table 1 that all indexes are with the limits permitted by the 1st grade GB8978 to 1996 standard (Shu et al. 2016; Wang et al. 2019). The lixivium concentrations of Ba and P are 0.04 mg/L and 0.46 mg/L, respectively, suggesting that calcination-modified treatment, the content of soluble phosphorus contained in PG, decreases and meets the standard requirements. The concentration of Ba in lixivium meets the environmental quality standards GB/T 14848-2017 (Quality standard for ground water. Class III). In conclusion, modified phosphogypsum-based embedded filler does not cause any secondary contamination.

Construction technology of the PGEF

The production practice and construction technology of PGEF are given in Fig. 7. Finally, steel-reinforced cages were prepared. Then, the PGEF was placed in the steel reinforcement cage, followed by pouring concrete using conveying pump to cover the PGEF. The construction of PGEF was completed. It can be concluded that the construction technology of PGEF has the advantages of simple process and easy operation.

Cost analysis for production of PGEF

Table 2 showed the cost and weight analysis of PGEF and commercial reinforced concrete. The cost of the PGEF and commercial reinforced concrete a monoblock the total cost were 4.73 CNY and 7.81 CNY, respectively. Each of them weights 30 kg and 90 kg, respectively. Thus, it is clear that the cost and weight of PGEF made in this research is much lower than that of same volume-reinforced concrete. The application of PGEF in floor structure exhibits excellent foreground.

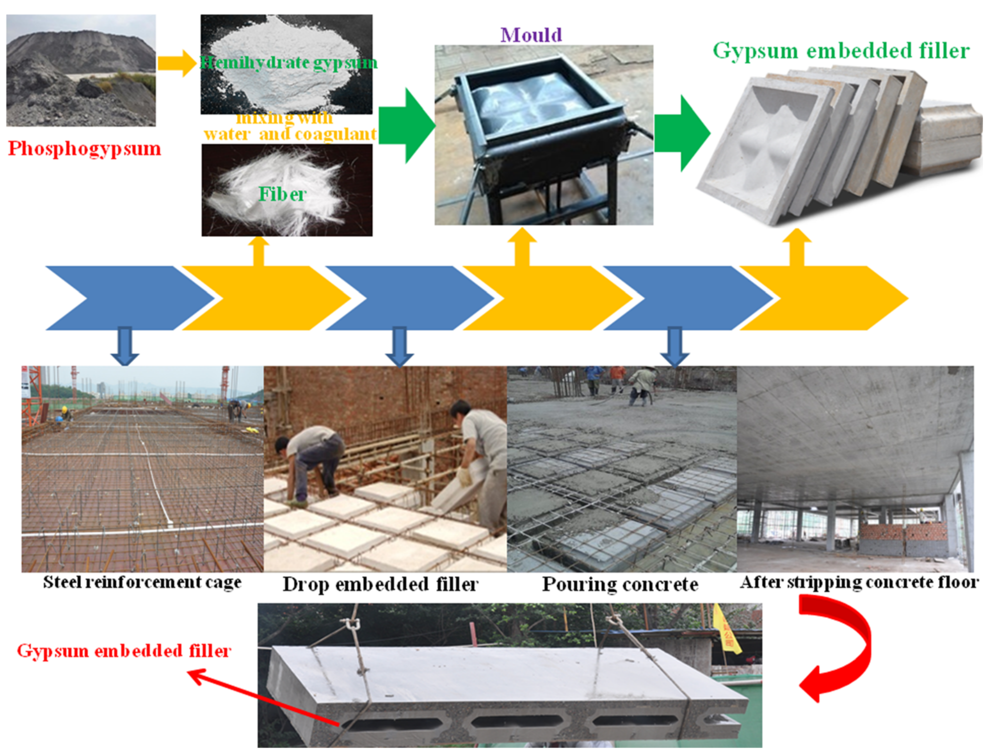


Fig. 7 Production and construction technology of PGEF

Table 2 Cost analysis for PGEF

Materials	Mix proportion (ton/a monoblock)	Price per unit (CNY/ton)	Cost of embedded filler (CNY/ton)
Modified phosphogypsum	0.3	280	84
Polypropylene fiber	0.005	11000	55
Coagulant	0.005	10000	50
Water	0.69	2.5	1.725
Total cost (CNY/ton)	189.1725		
Total cost (CNY/a monoblock)	189.1725 × 0.025(ton/a monoblock weight) = 4.73		
Weight of embedded filler	30 kg a monoblock		
Materials	Mix proportion (m^3/a monoblock)	Price per unit (CNY/ton)	Cost of commercial reinforced concrete (CNY/m^3)
Cement (P.O. 42.5)	12.1%	550	66
Aggregate	48 %	120	57.6
Sand	29.1%	150	43.7
Fly-ash	2.5%	160	4
Admixture	2%	2000	40
Water	7.3%	2.5	1.8
Total cost (CN/m^3)	213.1		
Total cost of the same volume-reinforced concrete (CNY/a monoblock)	213.1 × 0.03664(0.58 × 0.58 × 0.1m^3) = 7.81(without rebar)		
Weight of the same volume-reinforced concrete	90 kg a monoblock		

Conclusions

A novel construction material of (PGEF) was prepared, and it can be used in cast-in situ concrete hollow floor structure. The hydration–recrystallization action played a significant role in the development of basic physical properties of the PGEF. The engineering practice shows that the application of PGEF can markedly reduce the weight of the structures, and the steel and concrete consumption in buildings obviously decreases also. The cost of modified phosphogypsum-based embedded filler made in this research is far less than that of same volume of reinforced concrete. In addition, modified phosphogypsum-based embedded filler does not cause any secondary contamination.

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