Study on Physical and Chemical Properties of High Magnesium Nickel Slag-Phosphogypsum Composite Cementitious Materials in Different Particle Sizes

Sudong Hua\textsuperscript{1*}, Lili Zhang\textsuperscript{2}, Jian Zhang\textsuperscript{3}, Mingjing Jiang\textsuperscript{3}, Dapeng Guo\textsuperscript{3}, Fei Tong\textsuperscript{3} and Yihe Zhao\textsuperscript{4}

Abstract

High-magnesium nickel slag (HMNS) and phosphogypsum (PG) are hazardous industrial solid waste. The present work focuses on the feasibility of using the two materials as supplementary cementitious materials (SCM) added to cement. The slag and gypsum were ground into different specific surface area (2235 cm\textsuperscript{2}/g, 3040 cm\textsuperscript{2}/g and 3900 cm\textsuperscript{2}/g), then mixed into ten different samples. The effect of SCM addition was detected by isothermal conduction calorimetry (ICC) testing, compressive strength, mercury intrusion porosimetry (MIP), X-ray diffraction (XRD), scanning electron microscope (SEM) and linear shrinkage. The results showed that the HMNS-PG composite cementitious material with suitable specific surface area has relatively high activity, and a small amount of gel and alumina-ferric oxide-trisulfate (A\textsubscript{Ft} or ettringite) are detected in HMNS-PG composite cementitious material. According to the results, the high-magnesium nickel slag could be together with phosphogypsum as substitutes for cement, improved the utilization rate of industrial waste and reduced environmental pollution.

1. Introduction

During recent decades, a large amount of cementitious materials is consumed by those infrastructural constructions in the world, especially in China, and cement is the most widely used building material despite the large amount of energy consumed. For sustainability of ecology, energy and environment, and to reduce the CO\textsubscript{2} emissions (Shen \textit{et al.} 2015; Wu \textit{et al.} 2018; Yang \textit{et al.} 2015; Damineli \textit{et al.} 2010; Benhelal \textit{et al.} 2013), supplementary cementitious materials (SCM) are added to cement, it is well known as “blended cement” (Marsh and Day 1988). In recent years, a large number of researchers use coal-electric solid waste, metallurgical slag and industrial by-product gypsum as SCM (Pang \textit{et al.} 2013; Shi \textit{et al.} 2008).

High-magnesium nickel slag (HMNS) is a kind of metallurgical slag, it refers to an industrial waste discharged during the process of smelting nickel metal, which mainly contains SiO\textsubscript{2} and MgO. According to relevant statistics, over 20 million tons of HMNS is discharged every year in China. However, because of the physical and chemical characteristics of HMNS, such as low reactivity and poor wearability, the current utilization rate is not more than 10\%, mainly used in cement, concrete and other building materials industries (Kumer and Kumar 2017; Hua \textit{et al.} 2016). Recently some studies have also tried to use HMNS as geopolymer (Zhang \textit{et al.} 2017). The remaining large amount of unused HMNS occupies a large amount of land, although nickel slag is generally considered to be harmless, it is still potentially hazardous to the underground water. Some reports indicate that the leaching of solid wastes such as nickel slag by ICP-MS (Inductively coupled plasma mass spectrometer) method, the heavy metal content of some samples did not meet environmental standards (Yang \textit{et al.} 2014).

Phosphogypsum (PG) is by-product of the phosphate fertilizer industry, and its main chemical composition is CaSO\textsubscript{4}·2H\textsubscript{2}O. The utilization rate of PG in China is less than 10\%. About 280 million tons of PG waste is discharged every year in the world, and about 25 million tons is discharged annually in China. PG has similar properties to mining gypsum. Because of its characteristics, PG is not only used as an agricultural fertilizer, but also in the cement industry, building materials and road engineering (Wang \textit{et al.} 2016). However, due to the serious overcapacity of China's cement industry, with the gradual implementation of the national phase-out of cement production capacity and compression of cement production, as one of the cement production auxiliary materials, the preparation of cement retarder for phosphogypsum will also be affected. The latest research shows that phosphogypsum can also be used for soil improvement, and the improvement effect is remarkable (Enamorado \textit{et al.} 2014; Hentati \textit{et al.} 2015; Mao \textit{et al.} 2016). Similar to HMNS, a large number of PG also occupy a lot of open space, causing pollution to local groundwater (Li \textit{et al.} 2017; Papaslioti \textit{et al.} 2018).

\textsuperscript{1}Associate Professor, Nanjing Tech University, Nanjing, Jiangsu 211800, China.
\textsuperscript{*}Corresponding author, E-mail: huasudong@126.com
\textsuperscript{2}Engineer, Suzhou Concrete Cement Products Research Institute Co., Ltd., 215001, China.
\textsuperscript{3}Manager, Nanjing Pukou Urban and Rural Construction Group Co., Ltd,211800, China.
\textsuperscript{4}Manager, Suqian Huayi Concrete Co., Ltd, Suqian, Jiangsu 223839, China.
In the present study, a great deal of research has been devoted to using nickel slag as aggregate in concrete, and a small amount of research has been conducted on nickel slag powder as based material of geopolymer, but there has been little research on its application in SCM. Considering the relatively low activity of HMNS and PG, the effect of specific surface area on the activity of HMNS-PG composite cementitious materials was discussed by grinding the SCM and then passing through a 200 mesh, 400 mesh and 800 mesh screen (corresponding specific surface area is 2235 cm$^2$/g, 3040 cm$^2$/g and 3900 cm$^2$/g). The macroscopic properties of the samples were tested by compressive strength and linear shrinkage. Mercury intrusion porosimetry (MIP) testing, X-ray diffraction (XRD) testing, and scanning electron microscope (SEM) testing were used to detect the microstructure of the samples.

The alkalinity coefficient of HMNS is smaller than that of ground-granulated blast-furnace slag (GGBS), but its main mineral phase is similar to GGBS, mainly glassy phase. At present, studies have shown that HMNS can improve the resistance of concrete to chloride ion penetration. However, HMNS has the disadvantage of low activity. In view of the low calcium content of HMNS, industrial solid waste PG with high calcium content is introduced and ground to different particle sizes. This paper observes the reaction mechanism in a weakly hydrated environment to determine the potential activity of these two materials and whether they have a synergistic effect.

2. Experimental

2.1 Synthesis of blend cement binders

Prior to the preparation of the blends with cement, the PG and HMNS were ground by planetary mill, and then the two materials were sieved through a negative pressure screen. Following, the mixing proportions of the two materials and CEM 152.5 Portland cement and the physical characteristics of the produced blended cements are given in Table 1. The specific surface area is measured by BELSOR-MAX. The blend cement was dry mixed for 4 min and then mixed with water for 3 min. The liquid to solid ratio was set at 0.40 that gave an apposite flow-ability. The blend cement pastes were casted into 20 × 20 × 20 mm square molds for compressive strength test and 10 × 10 × 60 mm metal cuboid molds for linear shrinkage test. All binders were cured at 20 ± 2°C and RH > 95% in a temperature and humidity control room. After curing for 24 h, all the samples were de-molded for measuring initial strength.

2.2 Test Methods

2.2.1 Compressive strength

According to the Chinese standard GB/T 17671-1999 (similar to ISO 679:2009), the compressive strength of blend cement binders was measured by WHY-200 Auto Test Compression Machine at a loading rate of 1 mm/min. Each paste was tested for at least three duplicated samples to calculate an average value and standard error.

2.2.2 Isothermal conduction calorimetry testing

The exotherm during the hydration process of pastes was characterized by an external mixing procedure at 3114/3236 TAM 83 air isothermal calorimeter (thermal polymer AB) at 20°C for 168 hours. In order to reduce the impact of the temperature difference between the solid material and the machine on the exotherm, before testing the mixed raw materials were placed in an air-conditioned room at 20°C for at least 8 hours. The ratio of liquid to solid (mass) remained constant at 0.4.

2.2.3 Linear shrinkage

Linear shrinkage was tested using the cuboid specimens. Samples cured at 20°C was measured by using spiral micrometer from the de-mold time to 28 days. The samples were de-molded after curing at 20°C for 24 h, and the initial length of each sample was recorded immediately. Then, the samples were cured in a sealed bag at 20°C, and the linear shrinkage of the adhesive was calculated by equation (1):

$$\text{Lin}_{\text{drying shrinkage}} = (L_{in} - L_{de}) / 55 \quad (1)$$

where $L_{in}$ (mm) is the de-moulded length of each sample; $L_{de}$ (mm) is the measured length of each binder at a certain age; 55 (mm) is the effective length between the head nails of the specimen as casted.

2.2.4 Microscopic analysis

Powder samples were prepared for XRD analysis by
grinding the blend cement binders followed by oven-drying at 105°C for 6 h. To characterize the mineralogical compositions of the samples, D/MAX2500V (Rigaku) X-ray diffractometer was used at a scanning rate of 10 °/min with Cu Kα radiation, operated at 30 kV and 60 mA. The MIP testing which performed on pore-master GT-60 (Quantachrome) was used to analyse the pore structure of partial characteristic samples. The sample after the strength test were pulverized into small pieces having a diameter of about 5 mm, and the pieces were immersed in ethanol for 24 hours to stop hydration, and then dried at 60°C for 4 hours. The contact angle between the sample and mercury was set at 140° and the intrusion pressure ranged from 0.1 to 30 000 psi. the microscopic morphology of the sample was analyzed using ZEISS EVO MA18 scanning electron microscope (SEM).

### 3. Results and discussion

#### 3.1 Physical and Chemical Properties of raw materials

PG, obtain from Suqian Luling Chemical Co., Ltd. (Suqian, China) and HMNS, supplied from Jiangsu Delong Nickel Industry Co., Ltd. (Yancheng, China), were added to CEM I52.5 Portland cement. The chemical compositions of PG and HMNS, as analyzed by X-ray fluorescence (XRF), are shown in Table 2. The main chemical compositions of PG are CaO, SO₃ and SiO₂, and the main compositions of HMNS are SiO₂, MgO and Fe₂O₃. Table 3 gives a summary physical property for the two materials. Their particle size distribution was determined by a laser particle size analyzer, as shown in Fig. 1. The d₅₀ and d₉₀ of raw HMNS are 68.51 μm and 359.88 μm; while d₅₀ and d₉₀ of raw PG are 45.98 μm and 115.65 μm, the particle size of PG is smaller than that of HMNS, but both are relatively large.

The mineral components were investigated using X-ray diffraction (XRD). It can be seen from Fig. 2 that the result of XRD shown PG is well crystalline and HMNS is basically amorphous. Main crystalline phase in PG is gypsum, although PG contains impurities, the content of these impurities is lower than gypsum, and some of the impurities are amorphous, which makes it impossible to reflect these impurities in XRD diffraction peaks. A small amount of crystalline phases such as quartz and forsterite ferroan are observed in HMNS which means that the activity of HMNS is not high.

The PG and HMNS used in the experiment were ground by a planetary mill, and then the two materials were sieved through a negative pressure screen.

#### 3.2. Compressive strength

Figure 3 shows the compressive strength of SCM binders with curing at 20°C and RH > 95% for different curing days. Strength of the pure ordinary portland cement in 7 days reached 50.1 MPa, which is much higher than the result of the previous research (Vempati et al. 1994).

At all ages, the incorporation of PG (2235 cm²/g, 3040 cm²/g and 3900 cm²/g) influences the strength of the mixed cement, the strength decreases as the amount increases. After 7 days of curing, the incorporation of HMNS (2235 cm²/g, 3040 cm²/g and 3900 cm²/g) also reduced the strength of the mixed cement. The 7-day compressive strength of HMNS4-2 sample was 36.6 MPa and HMNS8-2 was 38.9 MPa, the latter is slightly

![Fig. 1 Particle size distribution of HMNS and PG.](image1)

![Fig. 2 XRD patterns of the HMNS and PG.](image2)
higher than the former. The compressive strength of cement HMNS4-2 reached 50.1 MPa, and the HMNS8-2 sample reached 57.9 MPa.

The reason should be considered from two aspects, part of high-mesh-number high-magnesium nickel slags participate in the formation of C-(M)-S-H and C-(A)-S-H gel by pozzolanic reaction, and the remaining irregular small particles of high-magnesium nickel slag can fill in pores, reducing porosity and making blend cement binders reaching higher strength (Bernal et al. 2016; Zhang et al. 2009; Papadakis et al. 1991). When incorporating nickel slag and phosphogypsum with low mesh number, the two SCMs exhibit different laws. Phosphogypsum of different mesh number has a little effect on phosphogypsum mixed cement. But the strength decreases obviously as the particle size of nickel slag decrease. The low mesh number nickel slag can also be used as a micro-aggregate although it hardly participates in the reaction. This system is also somewhat similar to the gap-graded blended cements (Zhang et al. 2011).

For PG-HMNS (PN) mixed cement, the compressive strength of mixed cement with 20% SCMs in 800 mesh (3900 cm²/g) is much higher than that with 20% SCMs in 200 mesh (2235 cm²/g) when it is cured for 7 days. As the curing age increased to 14 days, the gap becomes larger, and the strength of the PN4-2 is significantly higher than the PN8-2 and PN2-2. After 28 days of curing, the difference in compressive strength between the three binders decreased but the strength of the PN4-2 remains higher.

Presumably contribute to two kinds of reasons. First, high reticulated phosphogypsum (3900 cm²/g) slows down the process of early hydration. Second, the high specific surface area accelerates the process of reacting phosphogypsum with hydration products to form AFt, and an excessive amount of AFt is formed in the early stage, which causes expansion and thus destroys the structure. Subsequent micro-analysis will further determine which causes this phenomenon. The retardation effect of phosphogypsum with 400 mesh (3040 cm²/g) is not obvious, and it reacts with magnesium oxide, alumina in nickel slag (3040 cm²/g) and calcium hydroxide to form AFt.

### 3.3 Isothermal conduction calorimetry testing

**Figure 4a** shows heat evolution rates of blend cement binders with different SCMs at 20°C in the first 168 h. In each curve, a spike appeared immediately after mixing, and the coefficient of heat evolution reached a maximum at the same point in time of about 10 ~ 12 minutes. The spike corresponds to the combination of particle wetting and dissolution of solid materials. As the specific surface area of blend cement increases, the maximum heat release rate of the peak first drops and then rises. Probably because the SCMs with low mesh number and the cement do not mix well, resulting in better initial wetting and dissolution of the upper cement, and when the specific surface area reaches a certain value, SCMs can be well wetted and dissolved like cement. After the first peak, a brief “start” period can be observed within 2 h. The starting duration of paste mix with PG is shorter than pure cement. But HMNS-mixed cement delayed the process. Probably because PG dissolves better.

At ambient temperature, SCMs is less reactive than cement. After 2 h, the second exothermic peak is detected corresponding to mass production of the reaction products. The reaction of paste mixed with PG starts with a higher heat evolution rate. But the second peak amplitude is significantly lower than the HMNS-mixed paste. Its heat evolution rate is much lower than pure cement. In general, HMNS-mixed sample is more reactive than sample blend with PG.

**Figures 4b, c and d** show heat evolution rates of blend cement binders with addition of HMNS, PG and PN with different mesh number. It also shows that the first exothermic peak produced by the initial wetting dissolution. In addition, it can observe that PG-mixed cement dissolves faster than HMNS-mixed cement. After about 10 to 12 h, massive productions of reaction products are generated. In PG-mixed cement, as the specific space area of PG increasing, the heat evolution rate of the reaction decreases. While in HMNS-mixed cement, heat evolution rate of pastes with HMNS in 800 mesh (3900 cm²/g) is higher than in 400 mesh (3040 cm²/g), which indicates that the high specific surface area nickel slag has a certain activity. In HMNS-PG mixed cement, the hydration rate curves are almost the same. After 12 hours, the heat evolution curves of samples gradually approach each other.

**Figure 5a** shows the cumulative heat release of all binders in the first 168 h. From Fig. 5a, the cumulative heat release of HMNS-mixed cement is significantly higher than that of PG-mixed cement and PN-mixed cement. The early heat release of PG mixed cement is a little higher than PN-mixed cement because of particle wetting and dissolution of solid materials. In Figs. 5b, c and d, it can be seen that the cumulative heat release of mixed cement is lower than that of pure cement, it also
can be accounted for the incorporation of HMNS and PG reduces the activity of the cement (Mostafa and Brown 2005).

However, test results by Frias are different (Banfilla and Frías 2007), in their study, the addition of calcined paper sludge increases the hydration reaction rate, it may be associated with higher reactivity of SCM. In Fig. 5b, blend cement with 800-mesh HMNS (3900 cm$^2$/g) has higher cumulative heat release than with 400-mesh HMNS (3040 cm$^2$/g). Indicating that the increase of the specific surface area of the HMNS-mixed cement increases its reactivity.

While in Fig. 5c, contrary to HMNS, 800-mesh PG has lower cumulative heat release which also indicates that PG will slow down the progress of early hydration. The same situation as PG-mixed cement was observed in the cumulative heat release curve of cement blend with PN. However, the 7-day cumulative heat release curve of PN-mixed cement with different mesh number has almost no difference.

### 3.4 Pore structure

**Figure 6** shows the pore size distribution and pore structure of three different types of mixed cements: PG8-2, HMNS8-2, and PN8-2 and the reference one. The curve of pure cement exhibits a major pore size between 10 nm and 200 nm and the peaks is at about 28.0 nm, indicating the largest distribution at this pore size. The pores in the mesoporous interval of 10 to 200 nm accounted for 69.4% of the total porosity.

All curves of SCM mixed cement paste have a single peak distribution with different pore sizes: PG-mixed cement pore size range is 10 ~ 1000 nm while HMNS mixed cement range is 10 ~ 100 nm. The pore size range of PG-HMNS mixed cement is basically consistent with PG mixed cement. Meantime, it can be seen in the porosity diagram that the incorporation of PG increases the total porosity while forming more macropores (greater than 50 nm). The incorporation of HMNS reduces the total porosity and the number of macropores is also reduced. When PG and HMNS are incorporated into cement simultaneously, the total porosity and the rate of macropores remains high. That means engineering performance of blend cement binders mixed with PG is worse than HMNS-mixed cement.

**Figure 7** shows the pore size distribution and porosity of PG-HMNS mixed cement binders with 400 mesh (3040 cm$^2$/g) and 800 mesh (3900 cm$^2$/g). The pore size distributions of PN4-2 mixed cement and PN8-2 mixed cement are similar (both 10 nm to 1000 nm, with the
highest values being 139 nm and 150.9 nm) to those previously observed. Due to the negative impact of PG on pore structure, two different particle size of PN mixed cements have more harmful porosity and total porosity than pure cement. It should be noted that the number of macropores and total porosity of PN4-2 mixed cement is slightly lower than that of PN8-2. There are two reasons for this phenomenon. First reason is low-mesh-number high-magnesium-nickel slag has a better effect as a micro-aggregate in the mixed cement system, which has a weak positive influence on the pore structure and mechanical properties (including compressive strength) of the sample (Kuzielová et al. 2017). Another reason is that high-mesh phosphogypsum reacts with hydration products to form an excessive amount of AFt, the formation of AFt caused the system to swell, which destroyed the pore structure, and the analysis of the pore structure confirmed this conjecture.

Fig. 5 Cumulative heat release of the: (a) blend cement with different SCMs; (b) blend cement with incorporating different mesh number of SCM: HMNS; (c) blend cement with incorporating different mesh number of SCM: PG and (d) blend cement with incorporating different mesh number of SCM: PN.

Fig. 6 Pore structure of the Ref, PG8-2, HMNS8-2 and PN8-2 cured at 20°C after 28 d: (a) pore size distribution; (b) porosity.
3.5 Liner shrinkage

Figure 8 plots the linear drying shrinkage of blend cement binders curing in a temperature and humidity control room (20°C and RH > 95%). The linear shrinkage mainly occurred in early age (before 28 days). After 28 d, the degree of contraction slows down, so the figure only shows the linear shrinkage data for the first 28 d.

All samples exhibited a tendency to shrink throughout the process. The linear shrinkage of pure cement binders is in the range of 1.38 to 3.72 × 10⁻³ mm/mm, and the linear shrinkage of all the blend cement binders is less than 3.34 × 10⁻³ before 28 days, which is different with most geopolymer binders attribute to different systems (Zhang et al. 2018; Yang et al. 2014).

It can be found that the incorporation of SCM with different particle size into cement will reduces the linear shrinkage of the cement, and the degree of reduction is not same. PG-mixed cement has lower shrinkage than HMNS-mixed cement, because the previous reaction products such as calcium hydroxide, C-S-H and C-A-S-H gel react with CaSO₄·2H₂O to form AFt. It is well known that due to the slight expansion of AFt formation, it can compensate for the chemical shrinkage or drying shrinkage of blend cement binders to some extent. The linear shrinkage range of PN-mixed cement is 1.03 to 2.25 × 10⁻³ mm/mm, which is higher than PG mixed cement at the beginning and gradually lower than PG-mixed cement about 7 days later. It can be divided into two periods: the beginning is due to the loss of free water in the macropores and mesopores, which results in linear dry shrinkage. After 7 days, the expansion caused by the reaction to produce AFt compensates for partial shrinkage. The linear shrinkage of the binders with high specific surface area is also relatively low, probably because the evaporation of the water between the particles of the larger-sized admixture particles leads to the drying shrinkage of the system. According to the close-packing theory, the larger-sized admixtures fill the system, making the overall structure more compact.

3.6 XRD analysis

X-ray diffraction is used to identify phases formed during hydration. Figure 9 shows the XRD patterns of the blend cement binders with 20% amount and the refer-

![Fig. 8 Linear shrinkage of blend cement binders.](image)

![Fig. 7 Pore structure of the Ref, PN4-2 and PN8-2 cured at 20°C after 28 d: (a) pore size distribution; (b) porosity.](image)
ence sample curing for 28 days (Lothenbach et al. 2015; Zhao et al. 2016). The main hydration products including silicate, aluminate, calcite and magnesium phases such as portlandite, bluestone and lizardite are showed in the patterns. In reference sample, in addition to the calcium hydroxide, a small amount of carbonized calcium carbonate was observed due to carbonization with CO₂ in the air.

In HMNS8-2, PN8-2 and PN4-2 binders, the residual calcium hydroxide phase has a relatively low diffraction peak, and the diffraction peak of the raw material decreased or even disappeared, which means that the SCM addition has not delayed the evolution of hydration. In the pattern of PG8-2 binder, the diffraction peak of the raw material still exists although the diffraction peak of calcium hydroxide is lower. Because excess PG will reduce the rate of hydration, and a small amount of calcium carbonate formed was observed in both the reference and PG mixtures. In the pattern of HMNS8-2 binder, a small part of lizardite was detected due to pozzolanic reaction. HMNS with normal particle size is difficult to participate in the hydration reaction, but ultra-fine HMNS will partly participate in pozzolanic reaction. Compared to PG mixed cement, only a small amount of gypsum was observed in HMNS-PG mixed cement because gypsum (CaSO₄•2H₂O) reacted with hydration products and ettringite (AFt) is formed, while PG of higher mesh reacted faster and consumed more calcium hydroxide.

3.7 Microstructure

The microstructure of blend cement binders curing after 28 days are presented in Fig. 10. All the SEM photographs show a large amount of calcium hydroxide is produced during the hydration of cement. From Figs. 10b and c, a part of the HMNS having a high specific surface area reacts with calcium hydroxide and is then converted into products such as C-S-H, C-A-H gels. It can be seen that the pores of the mixed cement material are filled with a plurality of reticulated products. In Fig. 10c, due to the addition of PG, the previous reaction products such as calcium hydroxide, C-S-H and C-A-H gel react with CaSO₄•2H₂O to generate acicular AFt (Shen et al. 2009; Zhao et al. 2017; Cho et al. 2017; Guo et al. 2018; Shi et al. 2015). It is well known that due to the slight expansion of AFt formation, it can compensate for the chemical shrinkage or drying shrinkage of blend cement binders to some extent. Therefore, PG-mixed cement always has good volume stability. However, in Fig. 10a, an excess of acicular AFt is formed as an excess of high-mesh PG will react with the hydration product. In addition to the large amount of hydrated product, some HMNS particles that do not participate in the reaction can be observed from Figs. 10d and 10b. These particles hardly participate in the hydration reaction, but they can act as aggregates in the cementitious material system to fill the macropores and form compressive strength.

4. Conclusions

This study investigated the effects of different meshes of
high-magnesium nickel slag and phosphogypsum when used as SCMs on the thermal properties, composition and microstructure of cement paste. The following conclusions can be obtained.

1. In PG mixed cement, the early hydration process slowed down as the number of PG meshes increased. The XRD pattern of samples shows that part of Ca(OH)₂ reacted with gypsum to form needle-shaped AFt crystals. In HMNS mixed cement, a very small amount of Ca(OH)₂ reacted with the silica-alumina component to form a C-S-H gel after 28 days. More HMNS particles act as micro-aggregates to fill the macropores in the system and increase the strength of the system.

2. In the HMNS-PG composite cementitious material, higher mesh means slower reaction and lower strength. After curing for 14 days, PG will accelerate and participate in the reaction of Ca(OH)₂ and HMNS to form AFt. The 800 mesh (3900 cm²/g) composite cementitious material reacts to form an excessive amount of AFt compared with 400 mesh (3040 cm²/g), which destroys the structure of the system and reduces the strength of the mixed cement.

3. Although the compressive strength of high mesh HMNS mixed cement can reach nearly 90% of pure CEM 152.5 Portland cement, its grinding process consumes a lot of energy and the volume stability of the sample cannot be guaranteed. The results show that the 400 mesh HMNS-PG composite cementitious material reacts to form an appropriate amount of AFt crystals, which can slow down the linear shrinkage and ensure the mechanical properties of the sample. These results indicate that PG and HMNS are rich in elements such as silicon, magnesium and aluminum, which can be used to replace small part of cement like other SCM material, and even try to replace part of the cement to form new kinds of solid waste-based cementitious materials used as a road base material.

Acknowledgements
Funding from Jiangsu Higher Education Institutions for Priority Academic Program Development (PAPD, China), the Jiangsu Province Highway Science Research Program (grant NO. E3213010313201709126), the Jiangsu Province Science Technology Support Plan Project (grant NO. BE2017704), the Jiangsu Province University Natural Science Research Project (grant NO. 16KJB440001), the Jiangsu Province Social Development Project (grant NO. SBE2017740749), the Suqian City Social Development Project (grant NO. S201708) and the Jiangsu Provincial Department of Science and Technology Key Research and Development Program (Social Development) (grant NO. BE2018697).

References
Banfill, P. and Frias, M., (2007). “Rheology and conduction calorimetry of cement modified with calcined paper sludge.” Cement and Concrete Research, 37(2), 184-190.

Benhelal, E., Zahedi, G., Shamsaei, E. and Bahadori, A., (2013). “Global strategies and potentials to curb CO₂ emissions in cement industry.” Journal of Cleaner Production, 51(1), 142-161.

Bernal, S. A., San, N. R. and Van, D. J., (2016). “Alkali-activated slag cements produced with a blended sodium carbonate/sodium silicate activator.” Advances in Cement Research, 28, 262-273.

Cho, B. S., Lee, H. H. and Choi, Y. C., (2017). “Effects of aluminate rich slag on compressive strength, drying shrinkage and microstructure of blast furnace slag cement.” Construction and Building Materials, 140, 293-300.

Damineli, B. L., Kemeid, F. M., Aguiar, P. S. and John, V. M., (2010). “Measuring the eco-efficiency of cement use.” Cement and Concrete Composites, 32(8), 555-562.

Enamorado, S., Abril, J. M., Delgado, A., Mäs, J. L., Polvillo, O. and Quintero, J. M., (2014). “Implications for food safety of the uptake by tomato of 25 trace-elements from a phosphogypsum amended soil from SW Spain.” Journal of Hazardous Materials, 266(4), 122-131.

Frias, M. and Banfill, P., (2007). “Rheology and conduction calorimetry of cement modified with calcined paper sludge.” Cement and Concrete Research, 37(2), 184-190.

Guo, Y., Zhang, T., Liu, X., Tian, W., Chen, P., Wei, J. and Yu, Q., (2018). “The pore fillability of cementitious materials and its application in predicting compressive strength of gap-graded blended cements.” Construction and Building Materials, 168, 805-817.

Hentati, O., Abrantes, N., Caetano, A. L., Bouguerra, S., Gonçalves, F., Römbke, J. and Pereira, R., (2015). “Phosphogypsum as a soil fertilizer: Ecotoxicity of amended soil and elutriates to bacteria, invertebrates, algae and plants.” Journal of Hazardous Materials, 294, 80-89.

Hua, S., Wang, K. and Yao, X., (2016). “Developing high performance phosphogypsum-based cementitious materials for oil-well cementing through a step-by-step optimization method.” Cement and Concrete Composites, 72, 299-308.

Kumer, A. and Kumar, P., (2017). “Sustainable use of ferronickel slag fine aggregate and fly ash in structural concrete: Mechanical properties and leaching study.” Journal of Cleaner Production, 162, 438-448.

Kuzielová, E., Žemlička, M. and Bartoníčková, E., (2017). “The correlation between porosity and mechanical properties of multicomponent systems consisting of Portland cement–slag–silica fume–metakaolin.” Construction and Building Materials, 135, 306-314.

Li, X., Du, J., Gao, L., He, S., Gan, L., Sun, C. and Shi, Y., (2017). “Immobilization of phosphogypsum for cemented paste backfill and its environmental effect.” Journal of Cleaner Production, 156.
Lothenbach, B., Nied, D., L’Hôpital, E., Achiedo, G. and Dauzéres, A., (2015). “Magnesium and calcium silicate hydrates.” Cement and Concrete Research, 77, 60-68.

Mao, Y., Li, X., Dick, W. A. and Chen, L., (2016). “Remediation of saline-sodic soil with flue gas desulfurization gypsum in a reclaimed tidal flat of southeast China.” Journal of environmental sciences, 45(7), 224-232.

Marsh, B. K. and Day, R. L., (1988). “Pozzolanic and cementitious reactions of fly ash in blended cement pastes.” Cement and Concrete Research, 18(2), 301-310.

Mostafa, N. Y. and Brown, P. W., (2005). “Heat of hydration of high reactive pozollans in blended cements: Isothermal conduction calorimetry.” Thermochimica Acta, 435(2), 162-167.

Pang, X., Jimenez, C. W. and Iverson, B. J., (2013). “Hydration kinetics modeling of the effect of curing temperature and pressure on the heat evolution of oil well cement.” Cement and Concrete Research, 54, 69-76.

Papasioti, E. M., Pérez-López, R., Parviainen, A., Sarmento, A. M., Nieto, J. M., Marchesi, C., Delgado-Huertas, A. and Garrido, C. J., (2018). “Effects of seawater mixing on the mobility of trace elements in acid phosphogypsum leachates.” Marine Pollution Bulletin, 127, 695.

Papadakis, V. G., Vayenas, C. G. and Fardis, M. N., (1991). “Experimental investigation and mathematical modeling of the concrete carbonation problem.” Chemical Engineering Science, 46(1-2), 1333-1338.

Shen, W., Cao, L., Li, Q., Zhang, W., Wang, G. and Li, C., (2015). “Quantifying CO₂ emissions from China’s cement industry.” Renewable and Sustainable Energy Reviews, 50, 1004-1012.

Shen, W., Zhou, M., Ma, W., Hu, J. and Cai, Z., (2009). “Investigation on the application of steel slag-fly ash-phosphogypsum solidified material as road base material.” Journal of Hazardous Materials, 164(1), 99-104.

Shi, C., Meyer, C. and Behnoud, A., (2008). “Utilization of copper slag in cement and concrete.” Resources Conservation and Recycling, 52(10), 1115-1120.

Shi, M. X., Wang, Q. and Zhou, Z. K., (2015). “Comparison of the properties between high-volume fly ash concrete and high-volume steel slag concrete under temperature matching curing condition.” Construction and Building Materials, 98, 649-655.

Vempati, R. K., Rao, A., Hess, T. R., Cocke, D. L. and Lauer, J. H. V., (1994). “Fractionation and characterization of texas lignite class-F fly ash by XRD, TGA, FTIR and SFM.” Cement and Concrete Research, 24(6), 1153-1164.

Wang, L., Zheng, D., Zhang, S., Cui, H. and Li, D., (2016). “Effect of nano-SiO₂ on the hydration and microstructure of Portland cement.” Nanomaterials, 6, 241-256.

Wu, B. and Ye, G., (2015). “Development of porosity of cement paste blended with supplementary cementitious materials after carbonation.” Construction and Building Materials, 52, 52-61.

Wu, M., Zhang, Y., Ji, Y., Liu, G., Liu, C., She, W. and Sun, W., (2018). “Reducing environmental impacts and carbon emissions: Study of effects of superfine cement particles on blended cement containing high volume mineral admixtures.” Journal of Cleaner Production, 196, 358-369.

Yang, K., Jung, Y., Cho, M. and Tae, S. H., (2015). “Effect of supplementary cementitious materials on reduction of CO₂ emissions from concrete.” Journal of Cleaner Production, 103, 774-783.

Yang, T., Yao, X. and Zhang, Z., (2014). “Geopolymer prepared with high-magnesium nickel slag: Characterization of properties and microstructure.” Construction and Building Materials, 59(6), 188-194.

Zhang, T., Yu, Q. and Wei, J., (2011). “A new gap-graded particle size distribution and resulting consequences on properties of blended cement.” Cement and Concrete Composites, 33(5), 543-550.

Zhao, J., Wang, D., Yan, P., Zhang, D. and Wang, H., (2017). “Conversion of local industrial wastes into greener cement through geopolymer technology: A case study of high-magnesium nickel slag.” Journal of Cleaner Production, 141, 463-471.

Zhao, J., Wang, D. and Yan, P., (2017). “Design and experimental study of a ternary blended cement containing high volume steel slag and blast-furnace slag based on Fuller distribution model.” Construction and Building Materials, 140, 248-256.

Zhao, J., Wang, D., Yan, P., Zhang, D. and Wang, H., (2016). “Self-cementitious property of steel slag powder blended with gypsum.” Construction and Building Materials, 113, 835-842.