CHARACTERISTIC POLLUTANT PURIFICATION ANALYSIS OF MODIFIED PHOSPHOGYPSUM COMPREHENSIVE UTILIZATION

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Abstract
The waste product phosphogypsum (PG) is produced in phosphoric acid production processes. Its storage requires large amounts of land resources and poses serious environmental risks. In this work, detailed experimental research was carried out to investigate the potential reuse of PG after calcination modification as a novel building material for cast-in-place concrete products. The calcination modification mechanism was studied, and the environmental risk assessment of modified PG was presented. The results showed that the calcination modification includes crystal phase transformation, removal of impurities, and modifying the pH value. The calcination was carried out at 280 °C for 5 h, where the resulting product was a pH value of 7.1, and the soluble fluorine and phosphorus removal rates reached up to 69.2% and 71.2%, respectively. These removal rates met the requirements of the China national standard Phosphogypsum (GB/T 23456-2018). To ensure the environmental safety, ecological risk assessment methods for determining the leaching toxicity of the modified PG were employed. The toxicity of Ba and P elements in the modified PG products was assessed, as well as the leaching toxicity concentrations of all particular heavy metals, which were found well below the limits set by the national standards. All the results presented strongly suggest that the 280 °C modified PG presented here has excellent application potential as a raw component in building materials.

Keywords PG · Characteristic pollutants · Purification · Environment safety

Introduction
PG is an industrial by-product discharged during the wet production processing of phosphoric acid. At present, 90% of the phosphoric acid in the world is produced by wet processing, where nearly 5 t of PG is produced for every 1 t of phosphoric acid (Tayibi et al. 2009). The main component of PG is calcium sulfate dihydrate (CaSO4·2H2O), but it also contains a small amount of phosphate, fluoride, phosphoric acid, organic matter, and insoluble acid. At present, more than 500 million tons of PG is stored in China; the annual output is 76 million t, but only 31 million t are reused, leading to an

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annual utilization rate of only 39%. The unused PG is stored on-site, which not only occupies a lot of land, but also leads to serious safety problems and pollution of the environment. Several previous studies mainly focused on the reuse of PG in different fields such as its possible use as a backfill (Chen et al. 2017; Wang et al. 2009; Li et al. 2008), as a cement admixture or raw material (Shen et al. 2012, 2014; Taher 2007), as a concrete admixture (Alam et al. 2015; Huang et al. 2016; Nigade and Bagade 2015), as a mortar admixture (Mun et al. 2007; Yang et al. 2016; Bianca et al. 2021), as a brick admixture (Garg et al. 2011; Zhou et al. 2012, 2014), and as a raw material for ceramic tiles (Zhou et al. 2015, 2016). However, it has turned out in practice that it is hard to utilize PG on a larger scale due to the high processing and investment costs and secondary contamination, which explains the low utilization rate of only 39%. In particular, the environmental safety cannot be ensured, and a large-scale comprehensive utilization of PG is thus restricted. Therefore, finding solutions to consume PG on larger scales is a key research challenge. As a first step, high value-added utilization of PG in industrial demonstration projects has become a key task.

The core premise for large-scale and high value-added utilization of PG is a harmless pretreatment, because PG also contains harmful impurities such as phosphoric acid, fluoride, and organic matter, which need to be removed before PG can be directly reutilized. At present, the mainly processing steps of PG treating are as follows: (1) water washing: A large number of soluble impurities and organic matter in PG can be removed by water washing. However, the establishment of water washing production lines requires a large one-time investment, involves high energy consumption, and creates a sewage treatment problem. (2) Sulfuric digestion: PG is treated with sulfuric acid digestion and organic solvent extraction to remove the insoluble impurity such as quartz and inorganic. After purification, they can obtain high purity and high brightness anhydrous calcium sulfate. But, this process requires a large amount of sulfuric acid and organic solvent. (3) Lime neutralization can transform harmful impurities such as phosphorus and fluoride into inert insoluble salts to eliminate the adverse effects of these impurities in PG. This process may be the simplest; it needs the least investment, and leads to remarkable impurity removal efficiency. It is in fact the most widely used impurity removal and modification method at present, but it cannot eliminate the influence of organic matter on the performance of PG. Still, it is especially useful for PG with low organic matter content. (4) Ball milling: In general, the impurity removal effect of ball milling is rather unsatisfying, because it needs to be used in conjunction with other technologies and, thus, its application potential is limited. (5) Calcination: High-temperature calcination is the most effective method to remove eutectic phosphorus impurities in PG at present. Organic matter and soluble fluorine will be converted into gas for volatilization when calcined at high temperature (Taher 2007; Rashad 2015; Garg et al. 2011), which leads to the elimination of the adverse effects of organic matter and soluble fluorine on PG. From the above points, calcination modification technology is currently considered to be the most feasible and effective treatment method for PG.

The objective of this study is to investigate and evaluate the pollutant removal effect of calcined modified PG in detail, and to focus on the environmental risk assessment of calcined modified PG. The specific research contents are as follows: removal of impurities and changing the pH value and the basic physical properties of modified PG. Furthermore, to ensure environmental safety, a human health risk and ecological risk assessment method was adopted to assess the heavy metal content, and to further ensure the environmental safety of the modified PG product, we used sulfuric acid and nitric acid pretreatment for heavy metal extraction toxicity test method to assess the leaching toxicity of the modified PG product. All the results presented strongly suggest that the 280 °C modified PG presented here has excellent application potential as a raw component in building materials.

Materials and methods

Raw materials

Using phosphate fertilizer plant to provide modified PG in Chongqing City, China, the pitch diameter size (d50) was 42 μm, CaSO4·2H2O content was 92%, others are mainly solubilized salt and other impurities by XRF, and the water content was 14%. Fiberglass was sourced from a company in Chongqing City. Coagulant was Na2SO4, and was offered by a company in Chongqing City. The tap water was utilized for mixing.

Test methods

Basic experiment of calcining-modified PG

The PG should be uniformly distributed in the tray, and the thickness should not exceed 15 mm to ensure the uniformity of calcination. Then, the tray was placed in the blast drying box and calcined at 150 °C, 200 °C, 250 °C, and 280 °C for 5 h, respectively. The tray was naturally cooled to room temperature in the oven and removed.

The test of basic physical properties

The setting time of calcined PG was measured by JZ-HSO cement Vicat meter. The mechanical strength of calcined PG was measured by DKZ-5000 electric bending test machine and TYE-300 pressure test machine. The standard thickening water
consumption and 2-h strength of calcined PG were tested according to the method of *Calcined gypsum* (GB/T 9776-2008).

**Radionuclide limits**

The internal exposure index $I_{Ra}$ and external exposure index $I_r$ were expressed as the radionuclide limits; the calculation formula is shown below, and all the tests used the low background multichannel $\gamma$ spectrometer.

$$I_{Ra} = \frac{C_{Ra}}{200}$$

$$I_r = \frac{C_{Ra}}{370} + \frac{C_{Th}}{260} + \frac{C_K}{4200}$$

where $C_{Ra}$, $C_{Th}$, and $C_K$ were indicated as specific activity of radioactivity (Bq/kg) of Th-232, Ra-226, and K-40.

**The low background multichannel $\gamma$ spectrometer**

Using the FYFS-2002E automatic low background multichannel $\gamma$ spectrometer independently developed by Hubei Fangyuan Environmental Protection Technology Co., Ltd., and high resolution NaI (TI) detector design, radioactivity in building materials and products can be quantitatively analyzed.

**Thermal analysis**

The type of thermal analyzer is Netzsch STA449C comprehensive thermal analyzer produced by Niche, Germany, and the heating rate is 20 °C/min. At the same time, TG-DSC is used to analyze the mass change and heat absorption and desorption of calcined PG during heating.

**Soluble fluoride and phosphorus**

Soluble phosphorus was determined according to the gravimetric method in the China national standard: *Phosphate Rock and Concentrate-Determination of Phosphorus Pentoxide Content-Quinoline Phosphomolybdate Gravimetric and Volumetric Methods* (GB/T 1871.1-1995). Soluble fluoride was determined in accordance with the China national standard: *Phosphate Rock and Concentrate-Determination of Fluorine Content-Specific Ion Electrode Method* (GB/T 1872-1995).

**pH value**

The pH value of PG and modified PG was tested by a pH meter; the specific steps are as follows: weigh 10 g sample into a 200-ml beaker, add 50 ml distilled water, stir in the blender for 20 min, and let stand for 10 min. Then, the calibrated pH meter can be used to determine the pH value of the sample.

**Chemical composition**

Composition analyses of raw materials were tested by the XRF. The mineral structure of the samples was characterized by XRD (Physics Ultima IV, with Cu Kα radiation at a scanning rate of 80 per min in the 2θ ranging from 20 to 60°).

**Leaching property test methods**

Smash the samples and the grind them to the extent that they can sieve through the 3-mm sieve mesh. Then the powder was pre-treatment according to China national standard method *Solid Waste-Extraction Procedure for Leaching Toxicity-Horizontal Vibration Method* (HJ 557-2010), and then, running the test on the test machine, particularly pollutants, must satisfy the Chinese standard *Environmental Quality Standard for Soils* (GB15618-2018) and *Integrated Water Discharge Standard* (GB 8978-1996) to investigate the environmental security.

**Results and discussion**

**Basic performances of calcination modification PG**

**Optimal temperature for calcination modification**

By referring to the literature (Chen et al. 2017), CaSO$_4\cdot$2H$_2$O crystal in PG is in regular polygonal plate shape, and its shape is rather bulky. Therefore, in this section, PG was first dried at 50 °C temperature and then passed through 85 μm sieve for thermal analysis to determine the appropriate calcination temperature. The thermal analysis spectrum is shown in Fig. 1 below.

The thermal analysis temperature was set at 0–800 °C. It can be seen from Fig. 1 that the thermogravimetric analysis curve of original PG shows that it begins to dehydrate (free water) at about 50 °C, and continuously raised to about 100 °C; there is a relatively obvious weight loss, mainly due to the crystalline water in PG that begins to dehydrate gradually (Yassine Ennaciri et al. 2020); when the temperature is continuously raised to about 200 °C, the PG dehydration reaction leads to formation of the hemihydrate, and hemihydrate translates to anhydrate (Ankur and Dibakar 2020). PG gradually lost crystalline water, that is, there is a continuous weight loss phenomenon, and the weight loss rate was 19.8%. As it continues to heat up, the weight loss rate of PG remained and did not change much overall after heating to
about 800 °C. So, the preliminary optimal temperature for calcination modification is about 200 °C (Chen et al. 2018; Sheng et al. 2018).

Basic physical properties of calcination-modified PG

There are two aspects to consider, one is the calcination-modified crystal phase transform, and another is the pollutant removal, so three temperatures (150 °C, 200 °C, and 280 °C) were tested to research the related basic physical properties of calcination-modified PG.

PG was calcined at 150 °C, 200 °C, 250 °C, and 280 °C for 5 h, respectively. It can be seen from Table 1 that only after 280 °C calcination, the initial setting time and final setting time were 6.7 min and 28.6 min, respectively, and the 2-h flexural strength and compressive strength were 1.64 MPa and 3.10 MPa, respectively. All satisfied the China standard Calcined gypsum (GB/T 9776-2008); the basic mechanical properties of building gypsum powder can be met preliminarily. In addition, Jin et al. (2021) found that the temperature at which dihydrate gypsum is converted into β hemihydrate gypsum is 107–160 °C. Considering the decomposition temperature of soluble fluorine and phosphorus, the calcination modification temperature can be set at about 280 °C for PG.

Radionuclide limits

Radioactivity is a key indicator of PG resource utilization, especially for direction in civil architecture. So the specific activity of radioactivity (Bq/kg) of Th-232, Ra-226, and K-40 was tested and analyzed, and the analysis result is presented in Table 2. From Table 2, the radionuclide limits of $I_{Ra}$ and $I_{K}$ were 0.2 and 0.3, respectively, which completely met the Chinese standard requirements. That is to say, the calcination-modified PG can, as a raw material, be used for building materials.

| Table 1 Basic physical properties of calcination-modified PG |
|-------------------------------------------------------------|
| No. | Setting time (min) | 2-h strength (MPa) | Standard |
|     | Initial setting time | Final setting time | Flexural strength | Compressive strength |
| 150 °C calcination | 4.50 | 5.20 | 0.73 | 0.83 | Calcined gypsum (GB/T 9776-2008) |
| 200 °C calcination | 5.50 | 6.50 | 1.00 | 1.07 |
| 250 °C calcination | 6.20 | 7.10 | 1.32 | 1.91 |
| 280 °C calcination | 7.30 | 8.50 | 1.64 | 3.10 |
| Standard value (1.6 grade) | ≥ 3 | ≤ 30 | ≥ 1.6 | ≥ 3.0 |
Effect of calcination on appearance of PG

The PG dried at a low temperature of 80 °C was put into a crucible and moved into a muffle furnace for calcination to 280 °C with a heating rate of 5 °C/min and a holding time of 3–5 h. Then, it naturally dropped to room temperature. The final appearance of the PG after calcination is shown in Fig. 2 below. It can be seen that the color of original PG was dark gray. After drying at 80 °C, the color turned to bright gray. After calcining at 280 °C, the color turned to gray white, and the color gradually became light. That is, the PG calcined at 280 °C is suitable for use as building material (Contreras et al. 2018; Liu et al. 2019).

Effect of calcination on pH of PG

Original PG is a by-product of wet process phosphoric acid process in phosphate fertilizer plant. In addition to CaSO₄·2H₂O, there are acid substances such as phosphoric acid, hydrofluoric acid, and organic matter. Therefore, the pH of original PG measured in the experiment is 4.3, with strong acidity. If it is used as building materials, it needs to be used in a medium alkaline environment. The pH of PG after calcination pretreatment is shown in Fig. 3 below.

It can be seen from Fig. 3 that the initial pH value of original PG was 4.3 showing strong acidity; after predrying at 80 °C, the pH value was 5.2, which is improved; after calcining at 280 °C for 5 h, the pH value rises to 7.1. The reason is that calcium sulfate dihydrate lost free water and took away some acidic substances at 80 °C and the pH value rises. However, with the calcination temperature further rising to 280 °C, the acidic substances in PG began to volatilize or solidify, resulting in the pH value rapidly rising to 7.1, which was slightly alkaline. Therefore, it is very suitable to be used as the raw material for building materials.

Effect of calcination on soluble impurities in PG

Phosphorus and fluorine are the main impurities in PG, which are also the main factors affecting its performance. Phosphorus exists in soluble form, eutectic form, and insoluble form. Soluble phosphorus in PG mainly exists in three forms: H₃PO₄, H₂PO₄⁻, and HPO₄²⁻. Soluble fluorine is one of the main forms affecting the performance of PG. Impurity fluorine mainly exists in the form of NaF, Na₂AlF₆, and Na₂SiF₆, which can affect the setting time and compressive strength of gypsum-based materials (Ma et al. 2018; Radwan and Heikal 2005). Therefore, this section studied the influence of calcination temperature on the content of soluble fluorine and phosphorus in PG, and the specific test results are shown in Fig. 4 below.
It can be seen from Fig. 4 that with the increase of calcination temperature, the content of soluble fluorine and phosphorus in PG decreased significantly. Among them, soluble fluorine and soluble phosphorus decreased from 0.13 to 0.04% and 0.52 to 0.15%, respectively, with removal rates of 69.2% and 71.2%, respectively. The soluble impurity content calcined at 280 °C completely met the Chinese standard Phosphogypsum (GB/T 23456-2018); when PG is used as a gypsum building material product, the mass fraction of water-soluble P$_2$O$_5$ and fluorine is less than 0.8% and 0.5%, respectively. The main reason is that soluble fluorine and phosphorus are partly volatilized in high temperature environment, or transformed into inert insoluble substances, which makes their content greatly reduced. As such, water-soluble P$_2$O$_5$ will sublimate at 200–280 °C transforming into pyrophosphate, and HF in PG begins to volatilize at 112 °C. Especially when the temperature increases to 280 °C, the content of soluble phosphorus and soluble fluorine is very low.

### Key technology control of calcination PG

The harmless key technology of calcination modification pre-treatment is adopted. Specifically, the original PG was calcined in a rotary kiln with external heating source such as clean natural gas. The maximum temperature of calcination was raised to 280 °C, with a heating rate of 5 °C/min and a holding time of 5 h, and then, it was naturally cooling to room temperature. The pH value of the modified PG was close to medium alkaline, and the size of the crystal phase is greatly reduced from the large and regular polygonal plate to the small and regular columnar structure, which greatly improves its hydraulicity properties and possesses the excellent cementitious properties for preparing the high value and ecological utilization of by-product PG as a novel building material.

In addition, the tail gas treatment facilities of rotary kiln calcination are divided into three categories: dust removal, desulfurization, and secondary chamber combustion. Cyclone dust collector (dust removal efficiency is well) + pulse bag dust collector (dust removal efficiency is well and practical) and double alkali desulfurization (desulfurization and defluorination efficiency is well and practical) are mainly used. Also, the secondary chamber combustion further ensures the effect of tail gas treatment.

### Environmental safety performance test of modified PG

This paper mainly considered the characteristic harmful solubility elements Ba, P, and leaching toxicity of the heavy metals in the modified PG products. In addition, for further ensure the environmental safety, the ecological risk assessment method was adopted to assess the harmful elements’ security. The characteristic pollutants’ Ba and P test results are shown in Table 3.

The general aqueous solution leaching test results of characteristic harmful solubility elements Ba and P in calcined modified PG product are shown in Table 3. It is obvious that the concentration of soluble P is 0.42 mg/L, which meets the first-level standard of integrated wastewater discharge standard (GB 8978-1996) of 0.5 mg/L. Although there is no corresponding standard to control Ba, this study uses health risk assessment to assess its environmental safety risk as follows.

1. The determination of exposure dose refers to US EPA evaluation model and exposure parameters of Chinese population. The exposed population considers children and adults, respectively. The average life expectancy of people in Chinese is 77 years (a). The exposure of pollutants in water considers drinking and skin contact. The exposure dose is calculated according to formula (3) and formula (4).

\[
ADD_{dietary} = \frac{CW \times IR \times EF \times ED}{BW \times AT}
\]  

(3)
where ADD dietary refers to the drinking exposure dose, mg/(kg day). CW refers to the concentration of characteristic pollutant Ba, mg/L. IR refers to the intake rate of drinking water, 0.739 L/day for children and 1.478 L/day for adults. EF refers to the exposure frequency, both 365 day/a. ED refers to the exposure duration, 9 a and 30 a for children and adults, respectively. BW refers to the body weight, 30.4 kg for children and 59.2 kg for adults. AT is the average exposure time; the AT of children and adults are the same; the carcinogen is 74.75 × 365 days, and the non-carcinogen is ED × 365 days.

\[
ADD_{\text{dermal}} = \frac{CW \times SA \times PC \times ET \times EF \times ED \times CF}{BW \times AT} \tag{4}
\]

where ADD dermal refers to the skin absorbed dose, mg/(kg day). SA refers to the contact surface area of skin, taking 10,000 cm² and 12,800 cm² for children and adults, respectively. PC refers to the skin penetration constant of chemical substances, taking 0.000004 cm/h for barium. ET refers to the exposure time, both 0.22 h/day. CF refers to the volume conversion factor, \(10^{-3} \text{L/cm}^3\). CW, EF, ED, BW, and AT are the same as formula (3).

2. Health risk assessment

According to the classification of carcinogenicity of International Agency for Research on Cancer (IARC) and the database of Integrated Risk Information System (IRIS) of USEPA, it is determined that barium was a non-carcinogen. The calculation formulas of non-carcinogenic risk and total non-carcinogenic risk assessment model are shown in formula (5) and formula (6), respectively.

\[
R^n_i = \frac{ADD_i}{RFD_i} \times 10^{-6} \tag{5}
\]

\[
R^n_T = \sum_{i=1}^{j} R^n_i \tag{6}
\]

where \(R\) is the life-long risk of equivalent death from a particular adverse health effect, dimensionless, \(R^n_i\) is the non-carcinogenic risk, and \(R^n_T\) is the total non-carcinogenic risk; ADD\(_i\) is the average daily exposure dose of non-carcinogenic pollutants, mg/(kg·day); RFD\(_i\) is the reference dose for certain exposure routes of chemical contaminants, mg/(kg·day); for Ba, it is 0.2 mg/(kg·day) for drinking and 0.014 mg/(kg·day) for skin contact; \(1.0 \times 10^{-6}\) is the assumed acceptable risk level corresponding to RFD.

According to the calculated data in Table 4, it can be seen that the overall health risk value of Ba in modified PG product for children and adults is \(2.45 \times 10^{-8}\)–\(2.50 \times 10^{-8}\), which is far lower than the maximum acceptable risk level of \(1.0 \times 10^{-6}\) recommended by Swedish Environmental Protection Agency, Dutch Ministry of Construction and Environment and the British Royal Society. Therefore, the health risk caused by barium in the modified PG product is very low.

It can be seen from Table 5 that the heavy metals Cu, Zn, Pb, Cr, Hg, Ni, and As were detected under acid digestion pretreatment, while the heavy metal Cd was not detected in the modified PG product, and the detected heavy metal Cu, Zn, Pb, Cr, Hg, Ni, and As content all met the Soil Environmental Quality-Risk Control Standard for Soil Contamination of Agricultural Land (GB 15618-2018). However, in order to further ensure the product quality of the modified PG product, we used the single-factor index method and the potential ecological risk method of heavy metal pollution commonly used in the soil pollution control standard to determine the risk (Wang and Xiong 2021). The specific calculation is as follows.

1. Single-factor pollution index

Single-factor index (SFI) is a method that uses the ratio of measured value and standard value of a heavy metal in soil to determine whether this heavy metal has environmental safety risk. This method is also a common method to reflect the potential ecological hazards and risks of heavy metals. Taking the risk screening value in standard the Soil Environmental Quality-Risk Control Standard for Soil Contamination of Agricultural Land (GB 15618-2018) as the reference value (pH value is about 7), the single-factor pollution index (Pi) method was used to evaluate the risk level of heavy metal pollution in modified PG product. The calculation formula is as follows:

\[
P_i = \frac{C_i}{S_i} \tag{7}
\]

where \(P_i\) is the pollution index of heavy metal \(i\). \(C_i\) is the measured concentration of heavy metal \(i\). \(S_i\) is the reference value; the pollution risk classification standard of \(P_i\) is shown in Table 6. If the final \(P_i\) value is greater than 0.7, it means that this heavy metal has potential ecological hazards, and should be considered. Also, the results of single-factor pollution index calculated value are presented in Table 7.
2. Potential ecological environment risk method

The potential ecological risk method of heavy metal pollution was established by Swedish scientist Hakanson in 1980 according to the ecological benefits and environmental behavior of heavy metals (Wang and Xiong, 2021). This method can better reflect the potential ecological hazards of heavy metals. It is as follows:

$$RI = \sum E_r^i$$

$$E_r^i = T_r^i \times C_f^i$$

$$C_f^i = \frac{C_i}{C_i^0}$$

where RI is the potential ecological risk index. $E_r^i$ is the single potential ecological risk coefficient of heavy metal $i$. $T_r^i$ is the toxicity response coefficient of heavy metal $i$. $C_f^i$ is the single pollution coefficient of metal element $i$. $C_i$ is the measured heavy metal content of heavy metal $i$ in the model box; $C_i^0$ is the reference value of heavy metal $i$. The potential ecological hazard classification of heavy metals is shown in Table 8.

The evaluation includes eight elements: Cu, Zn, Pb, Ni, Hg, As, Cr, and Cd. In addition to the toxicity response coefficient of several elements given by Hakanson, the toxicity response coefficient of Ni was added according to the research results of Wang et al. (2022). Meanwhile, the screening value in the Soil Environmental Quality-Risk Control Standard for Soil Contamination of Agricultural Land (GB 15618-2018) was used as the reference value for the potential ecological risk assessment of heavy metals in modified PG product. The toxicity response coefficient and reference value of each evaluation factor are shown in Table 9.

From the test results of single-factor index method and potential ecological environment risk method in Tables 7 and 10, it is obvious that the calculated values of single-factor index of heavy metals Cu, Zn, Pb, Cr, Cd, Hg, Ni, and As in modified PG product are all lower than 1.0. The single ecological risk coefficients of the above heavy metal elements are all lower than 40 according to potential ecological environment risk method. Therefore, combined with the test results of both methods, the ecological environment risk of heavy metal pollution in modified PG product is very low.

To further ensure the environmental safety of the modified PG product, we used sulfuric acid and nitric acid pretreatment for heavy metal extraction toxicity test method. The test results are shown in Table 11. It can be seen that the leaching toxicity concentrations of all characteristic heavy metals are far lower than the China national standard: Identification Standards for Hazardous Wastes-Identification for Extraction Toxicity (GB 5085.3-2007). Therefore, to sum up, the calcined modified PG product of this research is an environment-friendly building material product.

| Table 5 | Test results of heavy metal content in products (mg/kg) |
|---------|----------------------------------|
| Test index | Modified PG product (mg/kg) |
|          | Cu  | Zn  | Pb  | Cr  | Cd  | Hg  | Ni  | As  |
| Measured value | 10.4 | 13.6 | 4.9 | 16.2 | ND  | 0.78 | 3.1 | 2.9 |
| Standard control value (GB 15618-2018) | 100  | 250  | 120 | 200  | 0.3 | 2.4  | 100 | 30  |

| Table 6 | $P_i$ pollution classification |
|---------|--------------------------------|
| Class   | $P_i$          |
| I       | $P_i \leq 0.7$ | Clean |
| II      | $0.7 < P_i \leq 1$ | Light |
| III     | $1 < P_i \leq 2$ | Low |
| IV      | $2 < P_i \leq 3$ | Medium |
| V       | $P_i > 3$     | High |

| Table 7 | Results of single-factor pollution index calculated value |
|---------|----------------------------------|
| Test index | Single-factor pollution index calculated value |
|          | Cu  | Zn  | Pb  | Cr  | Cd  | Hg  | Ni  | As  |
| Calculated value | 0.10 | 0.05 | 0.04 | 0.08 | —   | 0.33 | 0.31 | 0.10 |
| Class of pollution | I   | I   | I   | I   | —   | I   | I   | I   |

| Table 8 | Classification of heavy metal potential ecological risk |
|---------|----------------------------------------------------------|
| No.     | Potential ecological risk single coefficient | Risk grade |
| 1       | $E_i^r \leq 40$                  | Low   |
| 2       | $40 < E_i^r \leq 80$              | Medium |
| 3       | $80 < E_i^r \leq 160$             | High  |
| 4       | $160 < E_i^r \leq 320$            | Very high |
| 5       | $E_i^r > 320$                    | Extremely high |
Conclusions

This research has explained a series of studies done to evaluate the basic physical performances and characteristic pollutant purification of modified PG. The summary of the results obtained from the research is as shown below.

1. **PG calcined at 280 °C for 5 h** can obtain the pitch diameter size (0.5) of 42 μm; pH value was 7.1; the soluble fluorine and soluble phosphorus removal rates reached up to 69.2% and 71.2%, respectively, which can fully meet the requirements in national standard Phosphogypsum (GB/T 23456-2018). And the particle size of PG was greatly reduced, which greatly improved its hydraulic cementitious properties.

2. The harmless key technology of calcination modification pretreatment is adopted. The original PG was calcined in a rotary kiln under 280 °C, with a heating rate of 5 °C/min and a holding time of 5 h, and then, it was naturally cooling to room temperature, and the tail gas treatment facilities were divided into two categories: cyclone + pulse bag dust collector and double alkali desulfurization.

3. The ecological risk assessment methods for determining the leaching toxicity of the modified PG were employed. The toxicity of Ba and P elements in the modified PG products was assessed, and combined with the test results of both methods; the ecological environment risk of heavy metal pollution in modified PG product was very low. As well as the leaching toxicity concentrations of all particular heavy metals were also far below the limits set by the national standards.

Author contribution

Chao-qiang Wang: framework design, experiment, investigation, and analysis. De-ming Xiong: assisting with research and experiments and data analysis. Yu Chen: assisting with research and experiments and data analysis. Kai Wu: assisting with research and experiments and data analysis. Min-jie Tu: assisting with methodology and investigation. Pei-xin Wang: assisting with methodology and investigation. Zhao-ji Zhang: assisting with methodology and investigation. Lei Zhou: assisting with methodology and investigation. All authors read and approved the final manuscript.

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Data availability

All data generated or analyzed during this study are included in this published article.

Declarations

Ethical approval

This study does not contain any studies with human participants and/or animals.

Consent to participate

Written informed consent was obtained from individual participants.

Consent for publication

Not applicable.

Conflict of interest

The authors declare no competing interests.
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