

## A flotation combined extraction process for improving the whiteness of phosphogypsum

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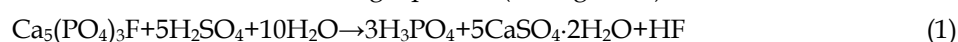
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**Abstract:** Every year, the production of industrial phosphoric acid generates more than 100 Tg of phosphogypsum (PG), leading to significant environmental damage and the occupation of a vast amount of land space. The urgent need to explore applications for PG has become increasingly apparent. However, impurities such as organic substances, slime, phosphorite, and SiO<sub>2</sub> reduce the whiteness of PG, making it difficult to utilize for high-value applications. To address this issue, this study employed a two-stage flotation process to remove the majority of impurities, including SiO<sub>2</sub>, organic substances, and fine slime adhered to the surface of PG particles. The raw PG sample was first sieved to remove some SiO<sub>2</sub> particles. After flotation, sulfuric acid and tributyl phosphate were introduced to decompose the PG particles and remove the impurities wrapped inside. Following this flotation combined extraction process, the whiteness of the PG sample improved from 54.1% to 92.9%, meeting the requirements for building walls and filters.

**Keywords:** phosphogypsum, whiteness, desilication, high-value utilization, floatation, extraction

### 1. Introduction

Phosphogypsum (PG) is a by-product of the phosphoric acid production process, where phosphate ore is reacted with sulfuric acid as shown in the following equation (Cheng, 2020):



The production of one Mg of phosphoric acid generates approximately 5 Mg of PG. Most PG is filtered out and stored, occupying a significant amount of land space and posing a risk of environmental damage (Zvimba, 2012; Yang, 2009; Xu, 2018). However, due to its poor whiteness and strength, only a small portion of PG is utilized for producing soil conditioner, gypsum building materials, and cement. Currently, the global PG stock has exceeded 6000 Tg, with China alone accounting for more than 400 Tg. As a result, the need to convert PG into high-value products has become increasingly pressing (Lysandrou, 2008; Rutherford, 1994).

Calcium sulfate with a whiteness exceeding 90% can be utilized as a filler material, and it is primarily obtained from natural gypsum (Ennaciri, 2019; Canovas, 2018). Although PG contains up to 85-88% calcium sulfate, converting PG to high-quality calcium sulfate can not only transform this solid waste into valuable products but also reduce the mining of gypsum ore (Wang, 2011; ALCORDO, 1993). However, PG typically contains various impurities such as organic substances, fine slime, silica, iron-containing compounds, and unreacted apatite (Mashifana, 2019; Zhou, 2019). As these impurities are present both on the surface and within PG particles, improving the whiteness of PG poses a significant challenge (Yang, 2017; Pérez-Moreno, 2018; Saadaoui, 2017; Chernysh, 2021).

In recent years, there has been a growing interest in purifying PG. Several methods have been widely used for this purpose, including washing, calcination, flotation, and extraction. Washing is a suitable method for treating PG with high organic content, which can improve the whiteness of PG. However,

this method is not very efficient on PG with high silicon content (Potgieter, 2003; Xiao, 2022). Calcination at a temperature above 800 °C can effectively remove impurities both on the surface and inside PG particles to obtain PG with high whiteness (>90%). However, the high energy consumption of calcination restricts its large-scale adoption. Flotation is a low-cost process that can remove silica and impurities adsorbed on the surface of PG particles (Jing, 2018). However, the improvement in whiteness after flotation is limited for PG with impurities inside the particles. Extraction methods for purifying PG are seldom reported, but some studies have shown that TBP is an excellent extractant for deep purification of PG due to its strong binding energy to silica and organic matter. Sulfuric acid combined with TBP extraction can remove impurities wrapped in PG, and the whiteness of the purified gypsum can reach more than 90%. (Zhao, 2017) Zhao used a single extraction process of sulfuric acid combined with TBP to treat phosphogypsum containing 5.82% SiO<sub>2</sub>. TBP and PG were then combined with 30 wt% sulfuric acid to obtain a mixture with a liquid-to-solid ratio of 5:1 (mass ratio) and a TBP-to-PG ratio of 5:1 (mass ratio). The whiteness of phosphogypsum increased from 50.67% to 92.05% after reaction at 90°C for 30min. It can be seen that although phosphogypsum with high whiteness can be obtained by this process, the consumption of tributyl phosphate will be increased if the flotation pre-removal of SiO<sub>2</sub> is not carried out. Hence, for PG with high silica content, a large quantity of TBP will be required without pre-desilication process, resulting in high costs. Because of the diversity in the chemical composition of PG, it is problematic to eliminate impurities with a single technique. Therefore, In order to improve the whiteness of phosphogypsum and reduce the cost, the advantages of flotation and extraction can be innovatively combined (Wang, 2020; Singh, 1993; Cao, 2022).

In this study, we report a flotation combined extraction process for enhancing the whiteness of PG. Before extraction, a large amount of SiO<sub>2</sub> and organic matter adhering to phosphogypsum surface were removed by low-cost flotation process. Subsequently, residual impurities wrapped in phosphogypsum were removed by combined extraction with sulfuric acid and TBP to achieve the purpose of deep purification and whitening. This process can effectively remove the impurities both on the surface of PG particles and enclosed in the PG particles (Mashifana, 2020), at the same time, the problems of high extraction solvent consumption and high cost are overcome when purifying high silicon phosphogypsum by direct extraction. which would guide the resource utilization of high-silica phosphogypsum.

## 2.1. Materials

The PG sample was obtained from Phosphorus Chemical Industry Co., Ltd., Yunnan Province, China.

The chemical composition analysis results of the PG sample are presented in Table 1. The results show that S and Ca are two main elements in the PG sample, accounting for 35.17 wt% and 25.80 wt%, respectively. Based on Fig. 1 and Table 1, the main impurity in the PG sample is SiO<sub>2</sub>, followed by Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, and Na<sub>2</sub>O.

Table 1. Composition of the PG sample

Compound	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	MgO	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Inorganic carbon
wt%	42.15	0.95	0.12	14.11	29.51	0.15	0.08	0.27	0.063	0.05

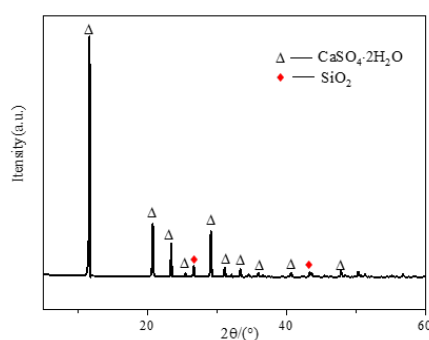


Fig. 1. XRD spectrum of the PG sample

The CaO, and terpenic oil were employed pH regulator, and frother, respectively. The laboratory-independently developed reagents YPN, a combination reagent based on mixed amine, was employed as a collector for SiO<sub>2</sub>, sulfuric acid was employed as a dissolving agent of PG. Tributyl phosphate (TBP) was used as an extraction agent. YPN, CaO and Sulfuric acid used in the work was of purity (AR) grade, YPN was purchased from the Chengdu Kelon Chemical Reagent Factory (Chengdu, China), NaOH was provided by the Tianjin Fengchuan Chemical Reagent Technology Co., Ltd. (Tianjin, China), terpenic oil used in the work is industrial grade. Furthermore, the tap water was used in all the experiments.

## 2.2. Methods

### 2.2.1. Classification test

In this study, a precise screening of multiple particle sizes of phosphogypsum was conducted using the EML 200 Premium Remote equipment from German manufacturer HAVER&BOECKER. Each screening utilized 300 g of phosphogypsum, with five different screen sizes employed: 0.15 mm, 0.074 mm, 0.045 mm, 0.038 mm, and 0.0308 mm. The amplitude and interval of the screening were set to 0.2 mm and 90 seconds, respectively. After the screening process was completed, the products of each particle size were dried in an oven, and their yields were determined through weighing. Subsequently, representative samples were prepared from each particle size, and their elemental distribution was analyzed using X-ray fluorescence spectroscopy (XRF).

### 2.2.2. Flotation tests

A 0.75 dm<sup>3</sup> XFD type flotation machine was employed to perform flotation experiments. In each flotation test, 250 g of sample was used. YPN is a highly effective collector for SiO<sub>2</sub> removal, but its performance is sensitive to the slurry's pH. Therefore, lime was added to adjust the pH before the flotation tests. Organic substances were removed using terpenic oil as the foaming agent and dosage was set at 400 g/Mg. The flotation test flow chart is presented in Fig. 3. The obtained products were dried using a laboratory oven and weighed on an electronic balance. Each set of experiments was repeated three times, and average values are reported. The flow chart of the flotation test is shown in Fig. 2.

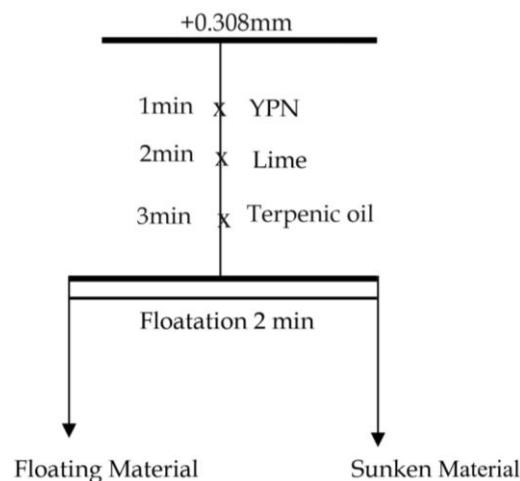


Fig. 2. Flow chart of the PG flotation tests

### 2.2.3. Extraction test

TBP was chosen as the extraction agent in this study due to its low water dissolution rate (0.1 wt%). The concentrate obtained from the flotation tests was dried and ground for 30 minutes. PG were then combined with 25 wt% to 35 wt% sulfuric acid and a certain amount of TBP is added to maintain a mass ratio of TBP to PG of 3:1 (mass ratio). The experimental setup is illustrated in Fig. 3. Next, 50 cm<sup>3</sup> of water phase liquid and organic phase liquid were transferred into a reaction beaker, and the electric stirring paddles were rapidly rotated to fully mix the organic and water phases. The extraction time was

0 to 90 minutes, and the extraction temperature was set to 25°C to 120°C. Once the reaction was completed, the liquid was poured into a separatory funnel for separation. The upper layer contained the organic phase with impurities, while the purified PG was in the lower layer (Zaheri, 2015; Zhang, 2014). After vacuum filtration and washing with deionized water, the purified PG product was dried in an oven at 40°C for 12 hours.

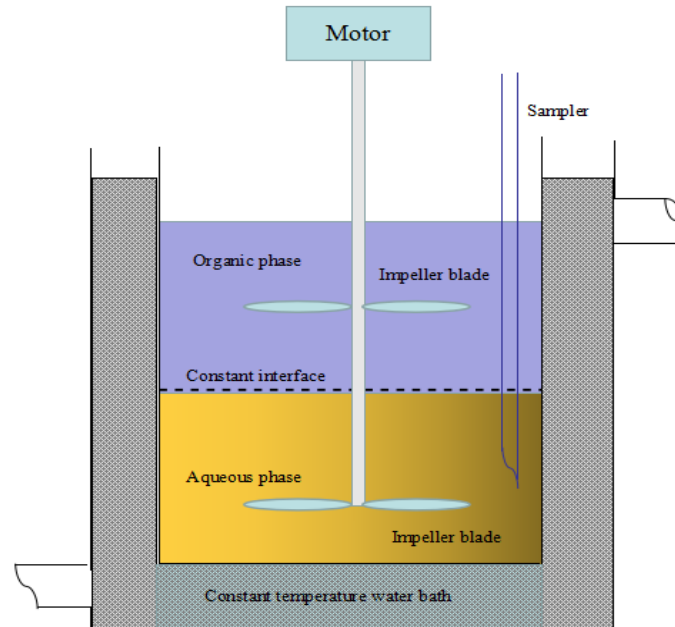


Fig. 3. Schematic diagram of the experimental setup

#### 2.2.4. Analysis

The whiteness measurement of the samples was performed using a WSD 3C whiteness colorimeter (Beijing Kangguang Optical Instrument Co., LTD.). The samples were first dried in an oven at approximately 40°C and then cooled to room temperature in the oven. Sample powder was prepared from three sample boards, and the average of the three sample boards was typically used. If the whiteness value of the three sample boards differed by  $\pm 0.5$ , the sample with the value closest to the average was selected, and the remaining two measurements were used to calculate the average whiteness value.

FESEM (Nova Nano SEM 450, USA) was adopted to examine the surface morphology of the PG samples. The samples were coated with platinum to enhance their conductivity (Dong, 2023).

The crystal phase of phosphogypsum samples treated by different methods was determined using an X'Pert3 Powder XRD system (Malvern Panalytical, Netherlands) with a  $\text{CuK}\alpha$  radiation of 1.5406 Å and a scanning speed of 0.2°/s (Cai, 2022).

### 3. Results and discussion

#### 3.1 Classification removal test of $\text{SiO}_2$

Table 2 presents the XRF analysis results of particles with different size ranges in the PG sample. Notably, the  $\text{SiO}_2$  content increases as the particle size decreases. For particles below 0.0308 mm, the  $\text{SiO}_2$  content reaches 37.01 wt%. To improve the desilication effect, particles below 0.0308 mm were removed from the PG sample before the flotation test. The screening results are shown in Table 3.

After screening the phosphogypsum using a 0.0308 mm mesh sieve, the results show an average yield of 83.67% and a  $\text{SiO}_2$  content of 9.62%. Compared to the raw phosphogypsum material before screening, the silica content decreases from 14.11% to 4.49%, which corresponds to a silica removal rate of 31.8%. These findings suggest that fractionating particle size to above 0.0308 mm is an effective method for removing silica from phosphogypsum. Therefore, to maximize silica removal and improve phosphogypsum whiteness, the 0.0308 mm particle size is selected as the flotation material.

Table.2. Compositions of the particles in the PG sample

Size/mm	Yield/%	Compound%					
		P <sub>2</sub> O <sub>5</sub>	MgO	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
+0.15	10.26	0.88	0.07	7.71	31.38	0.04	0.07
-0.15~+0.074	43.98	0.69	0.062	8.87	28.63	0.029	0.055
-0.074~+0.045	11.55	0.73	0.075	9.02	28.79	0.037	0.055
-0.045~+0.038	13.93	0.74	0.084	12.82	25.85	0.048	0.059
-0.038~+0.0308	3.97	0.82	0.115	15.62	25.62	0.077	0.064
-0.0308	16.31	0.64	0.134	37.01	17.89	0.139	0.118
totals	100.00	0.72	0.08	14.18	26.67	0.05	0.07

Table.3. Screening results of phosphogypsum

Times	Yield/%	P <sub>2</sub> O <sub>5</sub> %	MgO%	SiO <sub>2</sub> %	CaO%	Fe <sub>2</sub> O <sub>3</sub> %	Al <sub>2</sub> O <sub>3</sub> %
1	83.42	0.69	0.23	9.91	27.43	0.27	0.57
2	83.88	0.71	0.20	9.94	27.99	0.27	0.60
3	83.71	0.73	0.21	9.01	28.16	0.25	0.53
average	83.67	0.71	0.21	9.62	27.86	0.26	0.57

### 3.2. Flotation removal test of SiO<sub>2</sub> and organic substances

Fig. 4 shows the effect of the slurry pH on the yield and the SiO<sub>2</sub> grade of the processed PG. When the slurry pH is at 3 (acidic condition), the SiO<sub>2</sub> grade is 2.43 wt% and the yield is the lowest, 53.28 wt%.

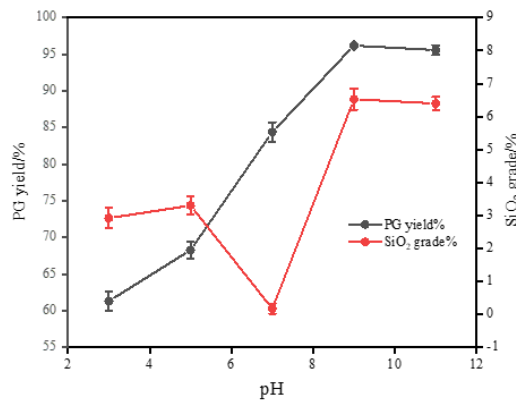


Fig. 4. PG yield and SiO<sub>2</sub> grade of the processed PG as a function of the slurry pH. YPN=350 g/Mg (The data points represent the mean values (n = 3 ± standard deviation))

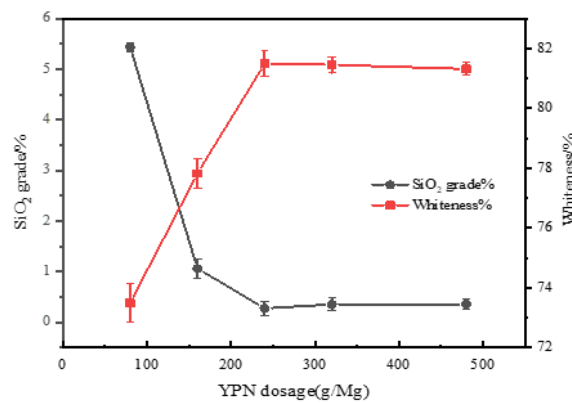


Fig. 5. SiO<sub>2</sub> grade and whiteness of the processed PG as a function of YPN dosage. pH=7 (The data points represent the mean values (n = 3 ± standard deviation))

When the slurry pH is 7 (neutral condition), the SiO<sub>2</sub> grade is the lowest (0.23 wt%) and the yield reaches 83.74 wt%. However, when the pH is above 7 (alkaline condition), the SiO<sub>2</sub> grade increase as the pH increases. Hence, the optimum pH of this reverse flotation process is 7.

Fig. 5 shows the effect of the YPN dosage on the SiO<sub>2</sub> grade and whiteness of the processed PG. the content of SiO<sub>2</sub> decreases dramatically when the YPN dosage increases from 100 g/Mg to 250 g/Mg. With the further increase of the YPN dosage to about 500 g/Mg, the SiO<sub>2</sub> grade does not show significant improvement(Li,2023). Based on these results, the optimum YPN dosage is 240 g/Mg, the grade of silica in the processed PG is the lowest, 0.24 wt%, and the whiteness is the highest, 81.89 %.

### 3.3. Optimization of the reverse flotation test

The optimized condition for the reverse flotation removal of SiO<sub>2</sub> is slurry pH=7 and the YPN dosage = 250 g/Mg. To further increase the yield rate and the quality of the processed PG, a two-stage flotation process is designed: rougher flotation and scavenger flotation. The flow chart of this process is shown in Fig. 6, and the results are shown in Table 4.

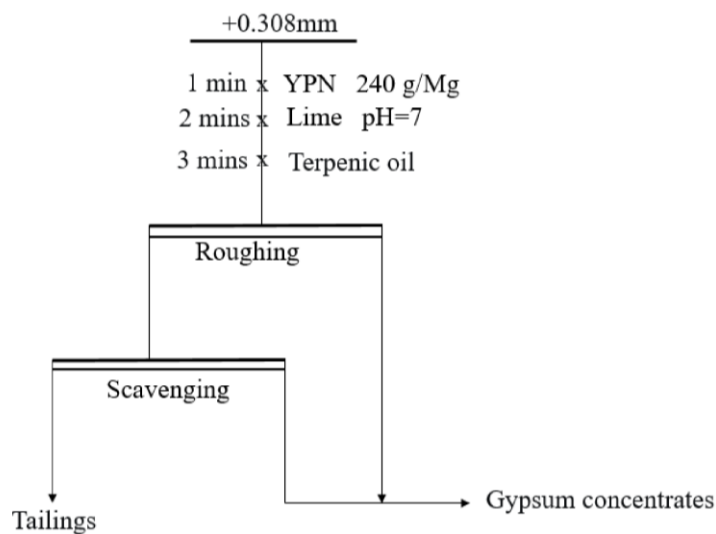


Fig. 6. Flow chart of the two-stage flotation process

Table 4. Results of the two-stage flotation process

Index Product	yield%	SiO <sub>2</sub> grade%	whiteness
Concentrate	86.97	0.79	81.51
Tailing	13.03	65.11	42.79

The two-stage reverse flotation process can efficiently remove SiO<sub>2</sub> and organic substances in the PG sample. The whiteness of the sample improved from 54.1% of the raw sample to 81.5% of the processed PG. However, flotation can only remove the impurities on the surface of the PG particles. Impurities wrapped inside the PG particles including silicon, aluminum, iron, and organic substances are unaffected during the flotation process. To further improve the whiteness of the PG, an additional extraction process is needed.

### 3.4. Performance of the extraction process

#### 3.4.1. Effect of sulfuric acid concentration on purified PG composition

The impact of sulfuric acid concentration on the composition of PG was investigated under the conditions of an extraction temperature of 90 °C, a liquid-solid ratio of 5:1, TBP/PG of 3:1, and a reaction time of 40 minutes. The concentration of sulfuric acid was varied from 0 wt% to 35 wt%. As shown in Fig.7, increasing the sulfuric acid concentration lead to a gradual reduction in impurities such as P<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub>, and MgO, which negatively affects the whiteness of the resulting PG. Specifically, when the sulfuric acid concentration increases from 10 wt% to 25 wt%, the content of P<sub>2</sub>O<sub>5</sub> decreases from 0.95 %

to 0.02 %, and the  $\text{Fe}_2\text{O}_3$  content decreases from 0.25 % to 0.01 %. Further increasing the sulfuric acid concentration does not significantly alter the quality of the resulting PG. Considering the overall processing cost, the sulfuric acid concentration was set at 25 wt%.

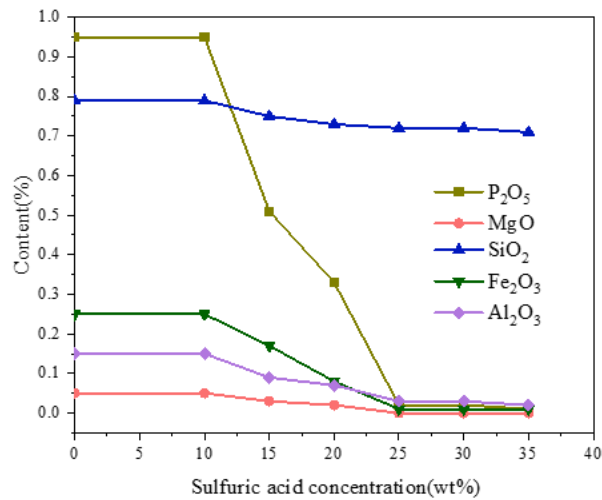


Fig. 7. PG composition as a function of sulfuric acid concentration

### 3.4.2. Effect of extraction temperature on the whiteness of purified PG

The impact of extraction temperature on the whiteness of the concentrate was investigated under the conditions of sulfuric acid concentration of 25 wt%, liquid-solid ratio of 5:1, TBP/PG of 3:1, and extraction time of 40 minutes by varying the extraction temperature from 25 °C to 120 °C. As shown in Fig. 8, the whiteness of the purified PG increased significantly with the rise in extraction temperature. At 25 °C, the whiteness is 81.93 %; however, when the temperature increases to 90 °C, the whiteness of the extracted concentrate reaches 92.9 %. Beyond 90 °C, the whiteness varies slowly with the extraction temperature. Therefore, the optimal extraction temperature is 90 °C.

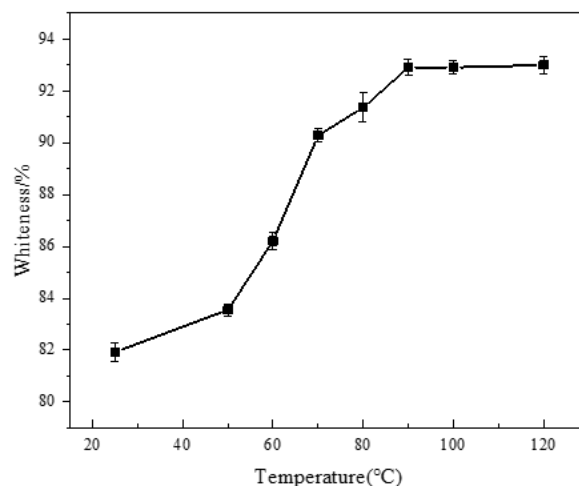


Fig. 8. PG whiteness as a function of extraction temperature

### 3.4.3. Effect of liquid-solid ratio on the whiteness of purified PG

Reducing the liquid-solid ratio is crucial for lowering energy consumption and increasing the processing capacity of purified PG. Therefore, it is essential to examine the effect of the liquid-solid ratio on the whiteness of the product. Under the conditions of a sulfuric acid concentration of 25 wt%, TBP/PG of 3:1, and an extraction time of 40 minutes, the liquid-solid ratio was varied from 1:1 to 10:1 by adjusting the amount of sulfuric acid solution. As shown in Fig. 9, the liquid-solid ratio had a negligible impact on the whiteness of purified PG. At a liquid-solid ratio of 1:1, the whiteness of the

purified PG was 92.77 %, whereas at a liquid-solid ratio of 10:1, the whiteness of the purified PG increased by only 0.14 %. However, at a liquid-solid ratio of 1:1, the slurry was too viscous, hindering processing efficiency. Therefore, the liquid-solid ratio was adjusted to 1:2 to allow for easier processing.

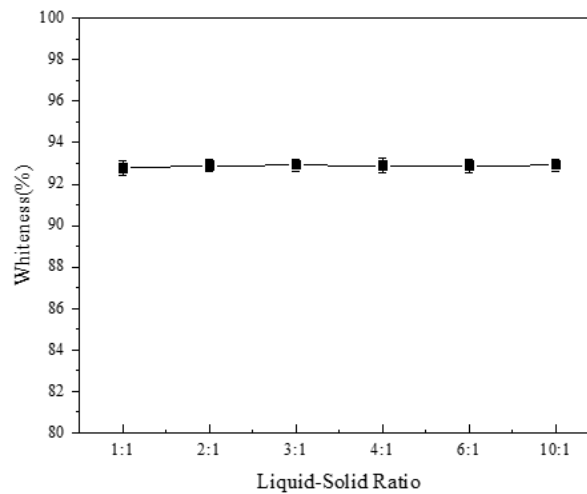


Fig. 9. PG whiteness as a function of liquid-solid ratio

#### 3.4.4 Effect of extraction time on the whiteness of purified PG

Shortening the extraction time is crucial for improving production efficiency. Therefore, it is necessary to examine the effect of the extraction time on the whiteness of the purified PG. Under the conditions of a sulfuric acid concentration of 25 wt%, liquid-solid ratio of 2:1, and TBP/PG of 3:1, the influence of the extraction time on the whiteness of the PG was investigated by varying the extraction time. As shown in Fig. 10, the whiteness of the resulting PG increases steeply with the increase in the extraction time and reached a plateau at around 40 minutes. Considering the processing efficiency, an extraction time of 40 minutes is selected for the subsequent study.

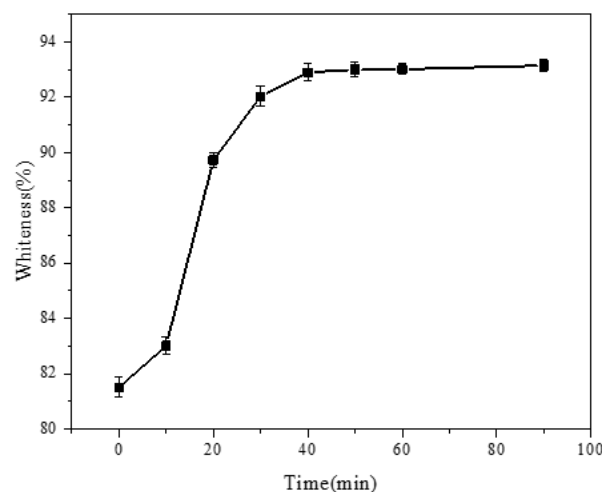


Fig. 10. PG whiteness as a function of extraction time

#### 3.4.5. Sample analysis

As shown in Table 5, the processed PG obtained from the two-stage flotation still contains impurities: 0.15 %  $\text{Al}_2\text{O}_3$ , 0.79 %  $\text{SiO}_2$ , 0.59 % F, and 0.25 % Fe. After the flotation concentrate is treated with sulfuric acid, some impurities affect the whiteness of phosphogypsum is reduced: the contents of  $\text{P}_2\text{O}_5$  is reduced from 0.94% to 0.02%, and the contents of  $\text{Fe}_2\text{O}_3$  is reduced from 0.25% to 0.01%, which indicates that sulfuric acid has the ability to dissolve apatite and iron impurities in the concentrate. But silicon and inorganic carbon, the main impurity affecting gypsum whiteness, the content of  $\text{SiO}_2$  only decreased from 0.79% to 0.72%, and the content of inorganic carbon only decreased from 0.0032% to



0.0030%, suggesting that silica and inorganic carbon could not be removed by sulfuric acid. When the flotation concentrate was extracted by sulfuric acid combined with TBP, the contents of these impurities are further reduced: The contents of MgO, Al<sub>2</sub>O<sub>3</sub>, and F are not detected, the content of SiO<sub>2</sub> is reduced from 0.79 % to 0.00 %, the content of P<sub>2</sub>O<sub>5</sub> is reduced from 0.94 % to 0.01%, and the content of Fe<sub>2</sub>O<sub>3</sub> is reduced from 0.25 % to 0.01 %. In addition, the composition of the extracted impurities also shows that the content of SiO<sub>2</sub> is as high as 68.27%, and the content of inorganic carbon increases to 0.59%, which indicates that the extracted impurities are mainly the remaining impurities SiO<sub>2</sub> and inorganic carbon in the concentrate. This suggests that after sulfuric acid removes impurities containing phosphorus and iron, TBP can further remove SiO<sub>2</sub>, which sulfuric acid cannot dissolve. The whiteness of the PG sample after the extraction process reaches 92.9 %.

Table 5. Multielement analysis of phosphogypsum flotation concentrate before and after extraction

Element	Chemical compositions							
	concentrate		Concentrate treated with sulfuric acid		Concentrate treated with sulfuric acid combined with TBP		the extracted impurities	
	Oxides/%	wt /%	Oxides/%	wt /%	Oxides/%	wt /%	Oxides/%	wt /%
P <sub>2</sub> O <sub>5</sub>	0.94	0.41	0.02	0.004	0.01	0.004	0.21	0.09
MgO	0.05	0.03	-	-	-	-	0.13	0.06
SiO <sub>2</sub>	0.79	0.112	0.72	0.336	0.00	0.00	68.27	32.61
CaO	35.21	24.50	35.23	25.16	37.51	26.78	4.53	3.02
Fe <sub>2</sub> O <sub>3</sub>	0.25	0.18	0.01	0.007	0.01	0.007	0.13	0.05
Al <sub>2</sub> O <sub>3</sub>	0.15	0.079	0.03	0.007	-	-	3.22	1.71
F	0.59	0.59	0.11	0.11	-	-	2.28	2.28
Inorganic carbon	0.0032	-	0.0030	-	-	-	0.59	-

- denotes that the contents were below the detection limit

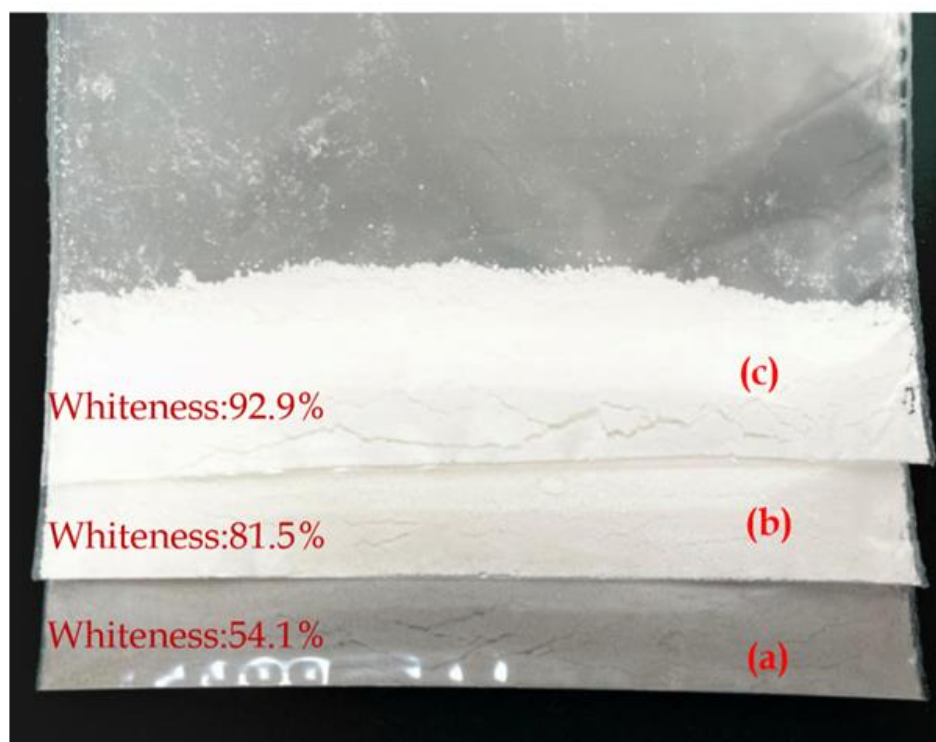


Fig. 11. Photographs of a raw PG sample (a), a processed PG sample after the two-stage flotation process (b), and a processed PG sample after the extraction process (c)

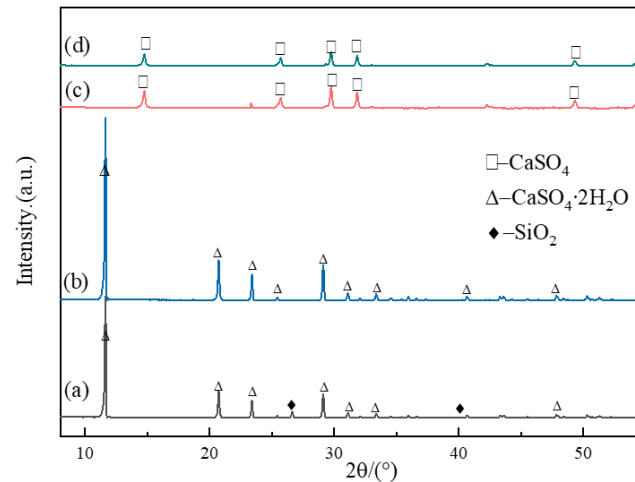


Fig. 12. XRD spectra of a raw PG sample (a), a processed PG sample after the flotation process (b), Flotation concentrate treated with sulfuric acid, (c), and Flotation concentrate treated with sulfuric acid and TBP extraction (d)

XRD analysis was conducted to investigate changes in the surface crystal structure of the PG sample following the two-stage reverse flotation, and the surface crystal structure of the flotation concentrate after sulfuric acid treatment and sulfuric acid combined with TBP treatment. As depicted in Fig. 12, the characteristic peaks of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{SiO}_2$  appear in the raw PG spectrum. After the two-stage reverse flotation, only  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  characteristic are observed in the XRD spectra, indicating successful removal of the majority of  $\text{SiO}_2$  and an improvement in the quality of the PG sample. When the flotation concentrate was treated with sulfuric acid, the characteristic peaks of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  disappear, and  $\text{CaSO}_4$  characteristic peaks are visible on the spectrum, indicating the chemical composition of the PG sample has been transformed from  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  to  $\text{CaSO}_4$ . When the flotation concentrate was extracted by sulfuric acid combined with TBP, the crystal phase of the obtained gypsum did not change, suggesting that sulfuric acid played a major role in opening gypsum crystals.

The SEM image (Fig. 13(a)) and EDX map (Fig. 13(b)) reveal that the surface of a raw PG particle is covered by small silica particles. After flotation, as illustrated in Fig. 13(c), the PG particle exhibits a smooth surface, indicating successful removal of surface-adsorbed silica particles, fine slime, and organic substances. Following the extraction process (Fig. 13(d)), the crystal morphology of the PG particles transforms into a sheet-like structure.

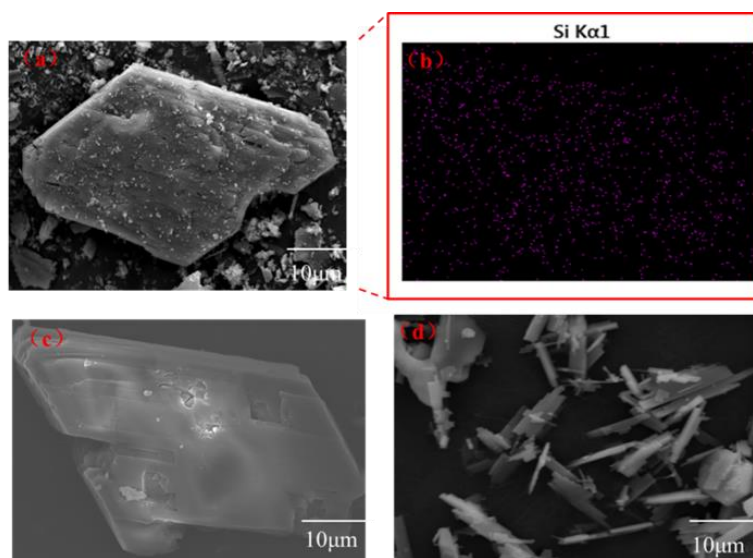


Fig. 13. SEM images of a raw PG sample (a), a processed PG sample after the two-stage flotation process (b,c), and a processed PG sample after the extraction process (d)

### 3.4.6. Effect of the purification method on the whiteness of purified PG

Raw PG samples have a black-gray appearance with only 54.1 % whiteness due to the presence of impurities such as silica, organic matter, and iron-phosphorus compounds, as shown in Fig. 14. Although the flotation process removes a significant amount of organic matter and silica, the whiteness can only be increased to 81.5 %. Furthermore, using the extraction process without flotation, the whiteness of phosphogypsum can only be increased to 86.5 %. To obtain PG with a whiteness greater than 90% through a single extraction process, the usage of TBP must be increased, resulting in high operational costs. However, by combining the low-cost flotation process with the extraction process to purify phosphogypsum, a significant amount of silica and organic matter can be removed during the flotation operation. This reduces the amount of TBP required in the subsequent extraction process. As a result, the whiteness of the gypsum can reach 92.9% with low TBP usage.

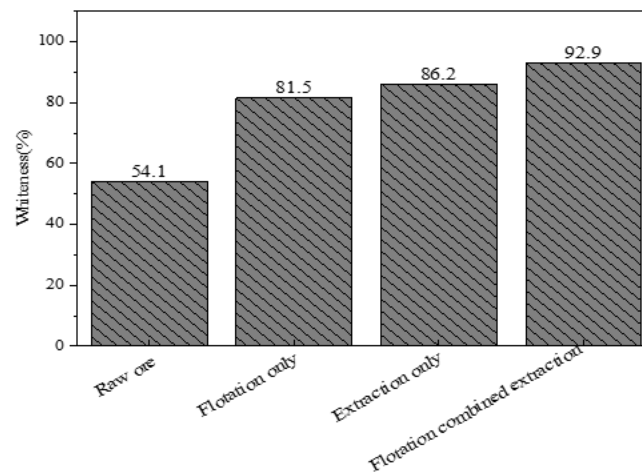
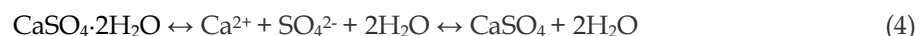


Fig. 14. Effect of purification method on the whiteness of purified PG

### 3.4.7. Extraction mechanism

During the extraction process, PG particles undergo decomposition and recrystallization in sulfuric acid, exposing impurities enclosed within (Eq. 4). The  $\text{Fe}_2\text{O}_3$  particles exposed during this process are then dissolved by sulfuric acid (Eq. 2, 3). Other impurities such as  $\text{SiO}_2$  and carbon that cannot be dissolved by sulfuric acid can be extracted using TBP (Christensen, 2008; Nie, 2020).

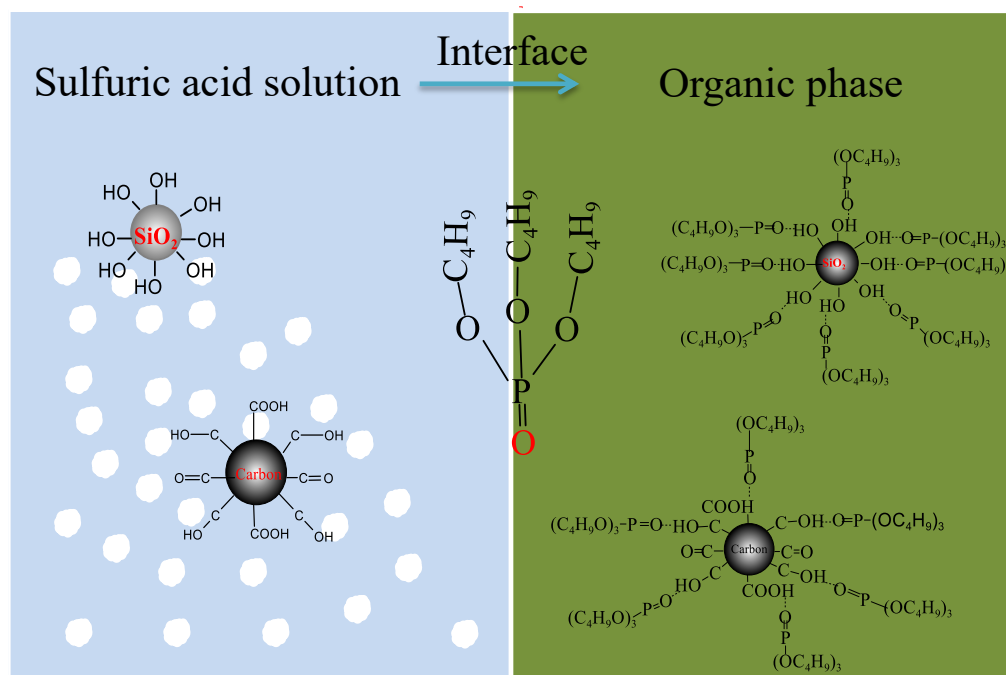


TBP is a potent Lewis base. The lone pairs of oxygen atoms in the  $\text{P}=\text{O}$  double bond of TBP have a high electron-donating ability and tend to form hydrogen bonds with molecules/surfaces containing hydroxyl groups. After exposing the impurities wrapped within PG particles, TBP forms complexes with  $\text{SiO}_2$  and carbon particles, which are then transferred into the organic phase.

## 4. Conclusions

This study has yielded the following conclusions:

1. Calcium sulfate dihydrate is the main component of the PG sample, which has a whiteness of 54.1% and a silicon dioxide content of 14.11%. Silica is mainly concentrated in particles below 0.0308 mm, with a content of 37.01%. Removal of particles below 0.0308mm resulted in a 4.49% of silica content and a removal rate of 31.8%.
2. A one-roughing-one-scavenging flotation process is used to reverse-flotation particles above 0.0308 mm, with the addition of terpeneol enhancing organic matter removal. The addition of  $\text{SiO}_2$  collector YPN at a dosage of 240 g/t to a neutral pulp system produces gypsum concentrate with a  $\text{SiO}_2$  content of 0.79% and a whiteness of 81.51%, resulting in a 27.41% increase in gypsum whiteness.



In this reverse flotation experiment, the application of neutral flotation can avoid the corrosion of over-acid and over-alkali on the equipment, making the industrial application easier.

- Most of the silica and surface-attached organic matter in PG are removed by flotation. The flotation concentrate is treated with sulfuric acid and tributyl phosphate. The addition of sulfuric acid dissolves Fe<sub>2</sub>O<sub>3</sub> and makes gypsum dihydrate undergo a dissolution and recrystallization process, exposing the impurities wrapped inside gypsum dihydrate, which are then removed through the complexation process with tributyl phosphate. Through this combined treatment, impurities adsorbed on the surface and wrapped inside the PG are removed, resulting in a whiteness of 92.9% and realizing the high-value utilization of PG.
- While the low-cost flotation process can eliminate a significant amount of silica and organic matter, other compounds containing iron and phosphorus, as well as silica and organic matter encased in the gypsum, are challenging to remove. Furthermore, the high content of silicon and organic matter in the PG sample limits the whiteness improvement of the gypsum without increasing TBP usage. To overcome this limitation, this study proposes an innovative approach that combines the low-cost flotation process with the extraction process to achieve deep purification of PG at a lower cost.

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