

Optimization of wet-process phosphoric acid for high-quality phosphogypsum

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Abstract: The chronic accumulation of phosphogypsum (PG) has resulted in significant environmental contamination issues within the wet-process phosphoric acid (WPPA) industry. An innovative technical route for transforming PG into a resource has been achieved through the introduction of floc flotation and acid cleaning in WPPA. The floc flotation using cationic polyacrylamide as a flocculant and micro lotion, which is composed of dioctyl phthalate, polyoxyethylene(10)nonylphenyl ether, kerosene, and n-octanol as a collector, has been performed. The effect of floc flotation on product quality and the underlying mechanisms were investigated by XRF, FT-IR, SEM, and 2-dimensional fractal dimension analysis. The optimal parameters were determined through a factor experiment, which yielded the following results: floc flotation temperature 65 °C, cationic polyacrylamide 180 g/Mg, collector 1.08 kg/Mg, and flushing sulfuric acid concentration 20%. The resulting PG exhibited a high grade of 95.01%, whiteness of 70.8%, and gypsum recovery of 93.52%. Furthermore, the soluble phosphorus and soluble fluorine levels are below 0.1%. In the flotation process, the combination of polyacrylamide and collector effectively separated fine organic matter and siliceous material with a hydrophobic bubble, facilitating their upward movement and subsequent separation from PG. The new WPPA, which exhibits enhanced product quality and reduced production costs, can be utilized extensively within the WPPA.

Keywords: phosphogypsum, optimization, purification, floc flotation, acid cleaning

1. Introduction

Phosphogypsum (PG) is a byproduct of sulfuric acid decomposition of phosphate rock to produce phosphoric acid (Rosales et al., 2020; Cuadri et al., 2021; Vasconez-Maza et al., 2021). The amount of PG rapidly increases at a rate of about 70 million tons per year, with a very low utilization ratio (less than 15%) in China (Zeng et al., 2021; Cao et al., 2022; Guan et al., 2022). In most industrial phosphoric acid production in China, the dihydrate process is used, which is 20% ~ 30% cheaper than the furnace-process phosphoric acid (Wang et al., 2011). The main chemical Eq. (1) of this process is as follows (Ennaciri et al., 2019).



However, a large number of harmful impurities in phosphate rock would enter phosphoric acid and PG, especially fluorine, which is difficult to separate once it enters the liquid phase. More seriously, according to Eq. (1), to produce 1 ton of phosphoric acid, approximately 5 tons of PG are yielded (Macías et al., 2017; Li et al., 2019; Men et al., 2022). These untreated PGs cause serious pollution and waste (Zhou et al., 2022; Shu et al., 2023).

The composition of PG is relatively complex, including not fully decomposed phosphate rock, residual phosphoric acid, fluoride, acid-insoluble matter, organic matter, etc. (Singh, 2002; Mi et al., 2019; Lv and Xiang, 2022). What's more, the existence of fluorine, phosphorus, and organic matter has the greatest impact on the resource utilization of PG. Therefore, removing impurities from PG in depth is the key technical problem of the comprehensive utilization of PG at present. Current research on PG mainly focuses on how to apply it to building materials. However, the defects that are difficult to overcome are the hazards brought by impurities in PG, such as the safety threat of radioactive elements or heavy metal elements (El Zrelli et al., 2019; Chernysh et al., 2021; Wu et al., 2022), the hazards of environmental dissolution of fluorine and phosphorus, and the degradation of material properties caused by organic matter and micro-grained gypsum (Moalla et al., 2018; Wang et al., 2022; Xu et al., 2022).

In other words, only by achieving the deep impurity removal and purification of PG can the value of PG be improved and its application be expanded. Nowadays, chemical, physical, and thermal processes are commonly used for PG purification. The chemical method is mainly acid leaching and neutralization (Guan et al., 2023). For example, citric acid or sulfuric acid solution has been used to transform F^- and PO_4^{3-} impurities into soluble substances (Liang et al., 2017; Salo et al., 2020; Cai et al., 2021; Xiang et al., 2023). It can be further eradicated through water washing and lime neutralization for solidifying PG pollution components (Mun et al., 2007; Liu et al., 2019a; Andrade Neto et al., 2021).

However, there are still many impurity components, such as F^- , PO_4^{3-} , SiO_2 , etc, after the washing process, facing high environmental risks after a long time. The physical method is mainly based on particle size or specific gravity separation, mainly including sieving and washing (Liu et al., 2019b). The purification equality of PG obtained by water washing is still low, and the water consumption is huge, so it is challenging to achieve water balance. The thermal method is mainly high-temperature calcination, which can effectively remove organic matters in PG and obtain hemihydrate/anhydrite, but it would consume a large amount of energy (Li and Zhang, 2021; Palla et al., 2022). Additionally, most of the processing process flows are complex, and the used PG comes from the waste solid from WPPA, which cannot solve the problems from the source, leading to the high treatment cost due to the storage and transportation (Wang et al., 2020; Li et al., 2023). These defects hinder the application of these technologies in industry. To reduce the cost, the purifying of PG in phosphoric acid production process may be the future direction.

The purification process of the PG mainly includes the improvement of the acid hydrolysis and filtration (Lokshin et al., 2013). In the acid hydrolysis stage, impurities can be reduced through measures such as improving phosphate rock quality, utilizing organic acids, implementing two-step acidification, selective acidification, adding surfactants, and adjusting reaction conditions (Lokshin et al., 2014; Hammas-Nasri et al., 2016). The complexity of practical application for improving the acid hydrolysis section lies in its harsh reaction conditions and high cost. Meanwhile, in the filtration section, impurities in PG can be eliminated via washing, pickling, increased flotation, and enhanced screening to render PG harmless (Moalla et al., 2017). Due to the higher content of impurities, the filtration process needs to multiple treatment, which also increase its complexity. At present, reports on the PG purification by foam flotation are gradually increasing. In 2020, a new method of PG purification, reverse positive flotation after quicklime pretreatment, has been reported to obtain purified gypsum with whiteness of 58%, purity of 96.6%, and recovery of 74.1% (Wang et al., 2020). Later, Zhang (Zhang et al., 2022) used tetradecyldimethylbenzylammonium chloride (TDBAC) for positive flotation to separate gypsum and quartz. The grade and recovery of gypsum can reach more than 90%. Fang (Fang et al., 2022) utilized reverse positive flotation to obtain purified PG with a whiteness of 63.42%, purity of 96.70%, and recovery of 85%. Du (Du et al., 2022) reported that purified PG with whiteness of 27.7%, purity of 92.54%, and yield of 94.9% can be obtained by reverse flotation of PG using methyl isobutyl carbinol as a collector to remove organic substances. Xiao (Xiao et al., 2022) obtained the purified PG with whiteness of 30%, purity of 98.94%, and recovery of 80.02% through direct positive flotation after classification pretreatment. However, the reported methods focused on the post-treatment of PG from the waste solid from WPPA, which cannot solve the problems from the source, leading to the high treatment cost due to storage and transportation (Tovazhnyansky et al., 2013). Therefore, purifying PG through direct

flotation of phosphate pulp can simplify the process further by reducing energy consumption and enhancing production efficiency.

Based on the above considerations, this work aims to obtain purified PG from the PG slurry in the phosphoric acid extraction tank by just adding a flotation device in WPPA. To clearly illustrate the difference, the traditional WPPA technique process (a) and the new strategy for WPPA (b) are presented in Fig. S1 in the Supplementary file. The influence of flotation temperature, collector, flocculant, and sulfuric acid concentration in acid pickling on the purification effect of gypsum has been investigated. Under the optimal conditions, the first grade PG for construction and crude phosphoric acid has been achieved, providing a simple and economical method for the resource utilization of PG, where the relative standard for the first grade can be seen in Table S1 in the Supplementary file.

2. Materials and methods

2.1. Materials and reagents

The wet phosphoric acid slurries were obtained from the Xiangyang Zedong Chemical Co., Ltd., Hubei, China, which were directly filtered to obtain old PG and old phosphoric acid, and the relative characterizations have been described in the discussion section for comparison.

The main chemical reagents were sulfuric acid (98%), cationic polyacrylamide (CPAM, Molecular weight is about 12 million), dioctyl phthalate, polyoxyethylene(10)nonylphenyl ether, dioctyl phthalate, n-octanol and kerosene which were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Sulfuric acid and n-octanol were analytical grades, and the others were industrial grade.

2.2. New strategy of the WPPA process

The new WPPA, including floc flotation and acid cleaning, is shown in Fig. 1, and the detailed procedure is presented below.

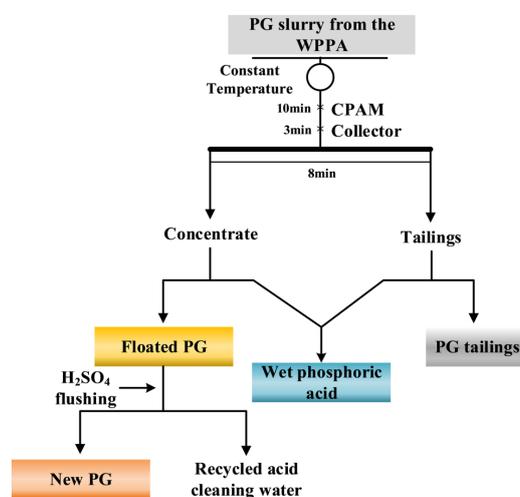


Fig. 1. Flowsheet of a new wet-process phosphoric acid

2.2.1. Flocc flotation

The 400 cm³ PG slurry with 30% pulp content in each experiment was added to the flotation cell of the XFD-500 flotation machine and stirred with the impeller speed of 1992 rpm. Dioctyl phthalate, polyoxyethylene(10)nonylphenyl ether, kerosene, and n-octanol were used to prepare a new micro lotion collector. Cationic polyacrylamide was used as a flocculant. First, the flocculant was added and stirred for 10 minutes, then the collector was added and stirred for 3 minutes, and finally, the air was blown and scraped for 8 minutes. The concentrate and tailings obtained from floc flotation were filtered and washed separately to obtain the floated PG and organic matter, and the filtrate was combined into wet-process phosphoric acid. Different floc flotation temperatures and dosages of reagents were set to

study their effects on the yield, recovery, grade, total phosphorus, total fluorine, soluble phosphorus, and soluble fluorine of floated PG and evaluate the quality of wet phosphoric acid.

2.2.2. Acid flushing test

The acid flushing test is the process of using diluted sulfuric acid to wash the floated PG. Typically, the floated PG obtained under the best conditions of floc flotation was washed with 100 cm³ sulfuric acid with different concentrations and dried, and the filtrate was recycled as an acid-cleaning solution.

Considering that the complex composition of PG is mainly solid phase and has appropriate fineness, it is the simplest method to achieve separation and purification by adjusting the difference of reactivity between gypsum and impurity components with sulfuric acid. The optimal conditions were determined by studying the effect of sulfuric acid washing with different concentrations on the quality of new PG.

2.3. Measurements and characterizations

The content of PO₄³⁻ and F⁻ was determined and calculated by quinoline phosphomolybdate gravimetric method and fluorine ion selective electrode method according to JC/T 2073-2011, respectively. The grade of gypsum was calculated based on the conversion amount of crystal water according to GB/T 23456-2018. The crystal water in gypsum was measured by the Guanya gypsum phase analyzer. The whiteness of gypsum was measured by the HYP-15 manual powder tablet machine and the WSB-2 desktop digital display whiteness meter. The quality of wet phosphoric acid was determined according to HG/T 4068-2008. Analysis of the main chemical components in gypsum samples was performed using the X-ray fluorescence method (XRF-1800; PANalytical B.V.). Spectroscopy measurements Fourier transform infrared spectra were measured by a Nicolet Nexus 670 FTIR spectrometer (Thermo Electron Corporation, America). The particle shape and surface morphology of gypsum samples were analyzed by scanning electron microscopy (SEM; EVO18, Germany). Flocculation properties were measured by fractal dimensions of the 2-dimension (Yang et al., 2013; Dai et al., 2023).

3. Results and discussion

3.1. Characteristics of sample

The main components in old PG were determined by XRD, which is shown in Fig. S2 in the Supplementary file. It showed that the main impurity in PG is quartz, along with high pollution components of P₂O₅ and F. The multi-element analysis results of old PG obtained through XRF and chemical examination are shown in Table S2 in the Supplementary file. The total fluorine (F), total phosphorus (P₂O₅), soluble fluorine and phosphorus contents in old PG are 1.2, 0.98, 1.07 and 0.72%, respectively. The loss on ignition (LOI) of the old PG was 18.9%, where 17.45% is crystalline water and 1.45% is organic matter. And the whiteness of old PG was 35.1%. The chemical composition analysis indicates that the purity of PG must be improved before reuse. It is beneficial to improve the whiteness and grade of the PG for better quality PG by removing the pollutant components. In addition, the composition analysis results, shown in Table S3 in the Supplementary file, of the old wet phosphoric acid show that it contained P₂O₅ 31.61% with a density of 1.62 g/cm³ and solid impurity indexes of 0.64%.

3.2. Floc flotation

3.2.1. Effects of temperature

Generally, the PG slurry from a phosphoric acid extraction tank has a relatively high temperature. In order to study the effect of temperature on the floc flotation of PG, different floc flotation temperatures of 65, 55, 45, and 35 °C were set, and the floc flotation experiments were carried out under the conditions of 180 g/Mg CPAM and 1.08 kg/Mg collector. The floc flotation results are shown in Fig. 2. In Fig. 2 (a), the recovery, grade, and whiteness of floated PG increased with increasing temperature. At 65 °C, the recovery, grade, and whiteness of gypsum reached 94.08, 96.6, and 71.95% respectively. In Fig. 2 (b), total phosphorus, total fluorine, soluble phosphorus, and soluble fluorine were the lowest at 65 °C. The whiteness at 65 °C is slightly lower than that at 55 °C, which can be attributed to the reduction of

flocculation caused by the hydrolysis of partial polyacrylamide at higher temperatures. With the increase in temperature, the grade of floated PG increased, the recovery changed little, the whiteness decreased slightly, and the total phosphorus, total fluorine, soluble phosphorus, and soluble fluorine were significantly reduced. It can be assigned to the high-temperature conditions because the phosphorus and fluorine existing in the gypsum solid solution will leach out into the liquid phase with the dissolution of gypsum. Therefore, high temperature was beneficial to improve the quality of floc flotation gypsum, and 65 °C should be selected as the suitable floc flotation temperature.

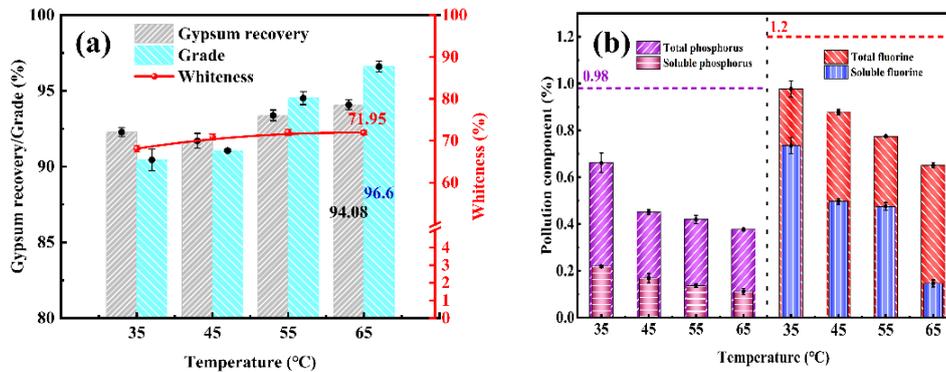


Fig. 2. Effect of temperature on grade, recovery, and whiteness (a), and pollution components (b) of the floated PG in floc flotation

3.2.2. Effects of flocculant dosage

Usually, the fine organic and argillaceous particles in PG were difficult to float, leading to the unsatisfactory effect of reverse floc flotation of PG. In this improved process, the addition of flocculant made the organic matter and fine argillaceous particles in PG form close flocs, which became easy to be removed by floc flotation. Not only did the whiteness of PG greatly improve, but also avoided and reduced the impurity entrainment of PG. Under the different dosages of flocculant CPAM as 90, 180, 270, and 360 g/Mg, the floc flotation tests under the condition of 65 °C and 1.08 kg/Mg collector were carried out. The results are shown in Fig. 3. In Fig. 3 (a), the whiteness, grade, and recovery of floc flotation gypsum are the highest when the dosage of flocculant is 180 g/Mg. In Fig. 3 (b), the total phosphorus, soluble phosphorus, and soluble fluorine of floc flotation gypsum are the lowest, and the total fluorine is relatively high at 180 g/Mg flocculant. With the increase of flocculant addition, the whiteness, grade, recovery, and total fluorine of floc flotation gypsum increased first and then decreased, while total phosphorus, soluble phosphorus, and soluble fluorine decreased first and then increased. The reason can be explained by the fact that when the flocculant is added excessively, the surface of mineral particles is saturated by the polymer molecules, and there is no adsorption vacancy on the surface of particles, which makes the flocculant lose its bridging effect. At the same time, due to the steric hindrance effect of the polymer molecular adsorption membrane, the particles repel each other, and the mineral particles were in a stable dispersion state again, making floc flotation effect performance worse. The increase in total fluorine was due to the electrostatic adsorption of fluosilicate in solution on the mineral surface by cationic flocculant. A small part of F will be adsorbed on the surface of floc flotation gypsum. The function of the flocculant is to absorb fine solid particles suspended in water through its polar groups, bridging particles. These aggregates have hydrophobic surfaces, which can combine with bubbles to float, resulting in effective separation with PG. When the flocculant is added to excess, it condenses particles into large flocculates through charge neutralization, resulting in sedimentation. Moreover, the hydrophilic surface of the particles formed by absorbing more flocculant molecules would lose the floatability. The results show that when the flocculant dosage is 180 g/Mg, the purification effect of PG is the best.

3.2.3. Effects of collector dosage

The key factor of floc flotation effect and cost is the collector dosage. Researchers had been sparing no effort in the pursuit of efficient and cheap collector formulations. The treatment cost had always been

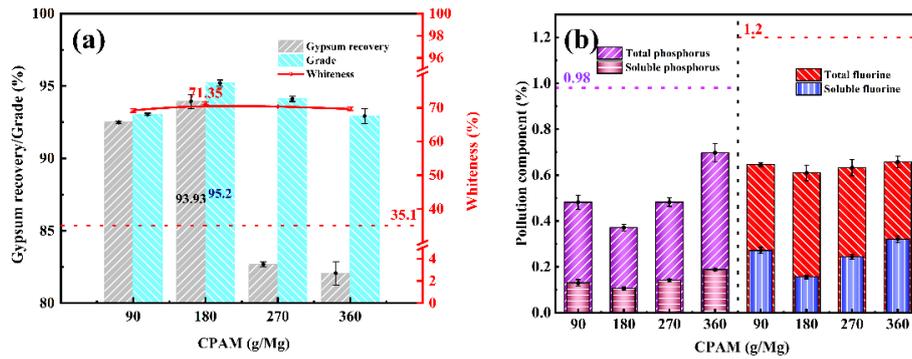


Fig. 3. Effect of flocculant dosage on grade, recovery, and whiteness (a), and pollution components (b) of the floated PG in floc flotation

the difficulty of PG purification. To reduce the cost, the formula has been optimized to improve the efficiency of the collector at the lowest amount of collector. The different dosages of collectors as 0.84, 1.08, 1.32, and 1.56 kg/Mg in the floc flotation test at 65 °C and 180 g/Mg CPAM were studied, respectively. The results are shown in Fig. 4. In Fig. 4 (a), the whiteness of floated PG was the highest at the dosage of 1.56 kg/Mg of collector, the recovery of floc flotation gypsum was the highest at the dosage of 1.08 kg/Mg of collector, and in Fig. 4 (b), the total phosphorus, total fluorine, soluble phosphorus and soluble fluorine of pollution components were the lowest at the dosage of 1.08 kg/Mg. With the increase of the amount of collector, the whiteness of floated PG increases, the recovery and grade increased firstly and then decreased, and the total phosphorus, total fluorine, soluble phosphorus, and soluble fluorine decreased firstly and then increased. The whiteness increase of floated PG was due to the impurity removal from its surface along with the increase of collector. It is noted that the gypsum recovery decreased suddenly when the dosage of the collector was 1.32 kg/Mg, along with the whiteness increase and grade reaching the highest when compared with those at 1.08 kg/Mg collector. It indicates that more impurities and some gypsums have been floated. It is because the hydrophobicity of the mineral surface increases when the dosage of the collector and this leads to excessive foaming. The increase of fluorine content was due to the adsorption of the collector and flocculant on the surface of the mineral particles on the fluorosilicate in the solution, especially when the collector is excessive, fluorine would enter the solid phase more, and the phosphorus content of the floated PG would not be affected. Therefore, 1.08 kg/Mg of collector dosage is the most suitable.

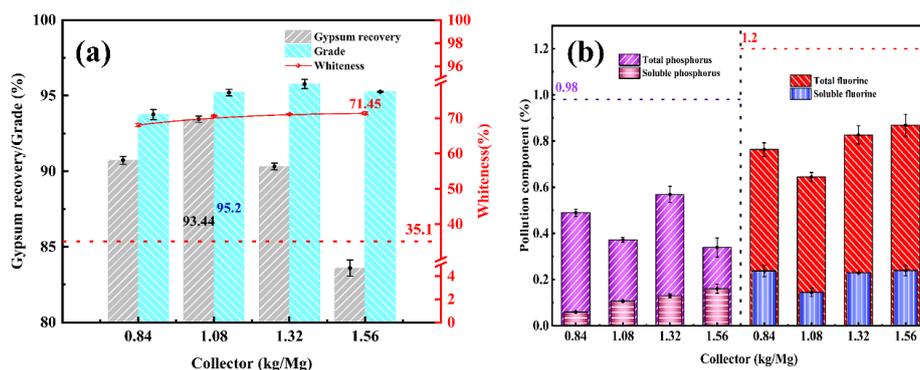


Fig. 4. Effects of collector dosage on grade, recovery, and whiteness (a), and pollution components of floated PG in floc flotation (b)

3.3. Acid washing

In WPPA, phosphoric acid is usually used to wash PG to recover phosphorus. Optimizing the washing process can further improve the quality of PG. The above results show that the pollution components are still high in the PG after floc flotation. To reduce the harmful components from PG, the sulfuric acid solution with concentrations of 0, 10, 20, and 30% was used to wash and purify the floated PG. The

obtained PG in each run is washed with sulfuric acid solution for the first time, and then water is used as the second and third washing medium to reduce the pollution component. The results are shown in Fig. 5. In Fig. 5 (a), the grade of new PG in the improved process is more than 95%, the gypsum recovery is more than 93%, and the whiteness is more than 70%. Compared with the PG obtained directly from flotation, the grade, recovery, and whiteness of new PG were affected less by acid washing. This is because the content of the pollution component is very low. Their removal would affect little to the grade, recovery, and whiteness. In Fig. 5 (b), the total phosphorus and soluble phosphorus of the pollution component decreased slightly, while the total fluorine and soluble fluorine decreased significantly. The results show that the fluorine is mainly adsorbed on the surface of PG as fine particles, which can dissolve or be decomposed with acid washing. As for phosphorus, most of them exist in the gypsum crystal in the form of heterogeneous isomorphism, and only a small part of the soluble phosphorus is dissolved with wolfberry soluble phosphorus. At the concentration of 20% sulfuric acid, the quality of new PG is improved much. New PG not only meets the Class I PG standard but also achieves the standard of GB18599-2020 "Class I general industrial solid waste", which improves utilization value greatly. The maximum recovery and whiteness for PG were 93.52 and 70.8%, respectively. Compared with the similar works reported in literatures, shown in Table 1, the recovery and whiteness of the new PG are the highest, indicating the higher efficiency of this work. The distinction between this work and previous studies is that PG was purified in the production process of phosphoric acid in this work, whereas other studies can be described as post-treatment. The new WPPA process makes full use of the heat source produced in the wet-phosphorous acid, decreasing the cost for further treatment of PG.

Table 1. Comparison of the effect of different treatment methods

Method	Reagents	Recovery	Whiteness	References
Grading and flotation	Mixed amine, sodium silicate, pine	80.02%	37.05%	(Xiao et al., 2022)
Sieving and acid leaching	Sulfuric acid	-	-	(Ennaciri et al., 2019)
Reverse-direct flotation	Kerosene, pine oil, alkyl, ether amines	85%	63.42%	(Fang et al., 2022)
Reverse-direct flotation	Lime, dodecyltrimethyl ammonium chloride, Pine oil	74.1%	58.4%	(Wang et al., 2020)
Reverse-direct flotation	KH, dodecylamine hydrochloride, cetyl trimethyl ammonium bromide	79.48%	69.2%	(Qi et al., 2023)
Grinding	Span-80, TX-100, and Tween-80	-	51.9%	(Chen et al., 2023)
Reverse flotation and pickling	Cationic polyacrylamide, dioctyl phthalate, polyoxyethylene(10)nonylphenyl ether, kerosene and n-octanol	93.52%	70.8%	This work

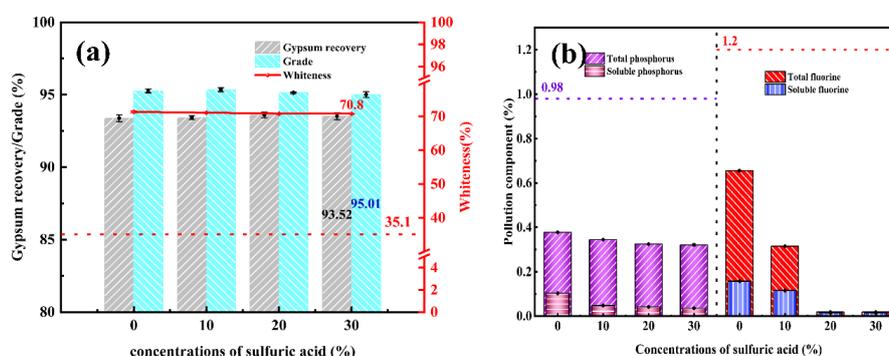


Fig. 5. Effects of sulfuric acid concentrations on grade, recovery, and whiteness (a), and pollution components (b) of new PG in acid washing

3.4. Fractal dimension of flocs mechanism exploration

Based on the above experiments, the flocculation mechanism of the improved process is shown in Fig. 6. For 2-dimensional flocs, the smaller the 2-dimensional fractal dimension D_2 , the looser and more open the floc structure. The closer the D_2 value is, the denser the floc structure is. Fig. 6 (a, b) are the images of old gypsum and PG after flocculation with 0.3% concentration flocculant, and Fig. 6 (c, d) are their respective projected area and characteristic length logarithms. The 2-dimensional fractal dimension of the floc was obtained by linear fitting. A comparison of Fig. 6 (a, b) reveals that the addition of flocculant causes PG to undergo polymerisation from dispersed particles to flocculent groups, resulting in a significant reduction in the concentration of fine particles. Concurrently, a considerable quantity of diamond-shaped gypsum can still be seen in Fig. 6 (b), indicating that flocculation has little impact on the gypsum itself. Fig. 6 (c) shows that the 2-dimensional fractal dimension of the floc formed by the old gypsum's colloid is 1.67 ± 0.02 with a fitting curve R^2 of 0.9351. Fig. 6 (d), shows that the 2-dimensional fractal dimension of the floc formed after adding flocculant is 1.76 ± 0.02 , and the fitting curve R^2 is 0.95887. The higher D_2 indicates that by adding flocculant, the organic matter and siliceous fine particles in PG form a dense floc through adsorption bridging and net trapping and sweeping, which made PG change from a dispersed mixture to a complex phase of PG and flocculent, which is easier to be separated by floc flotation.

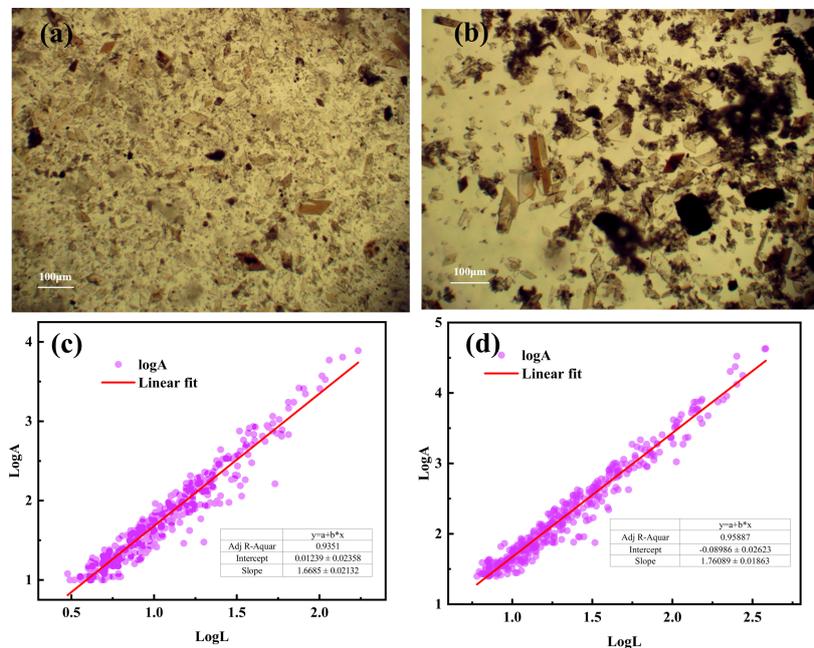


Fig. 6. (a) Old PG, (b) PG in 0.003% CPAM, (c) The log-log plots of A and L of old PG; (d) The log-log plots of A and L of PG in 0.003% CPAM

3.5. Results of solid product

3.5.1. Component analysis of solid products

The main purpose of this process is to obtain purified PG products. Therefore, the composition analysis and comparison of the old PG, floated PG, PG tailings, and new PG were carried out, and the results are shown in Table 2. It can be seen that the content of F, P, alkali metal, silicon dioxide, and sesquioxide in the floc flotation PG was greatly reduced, while the content of various impurity elements in the PG tailings was significantly increased, and the content of pollution components in the new PG was further reduced. By optimizing the process, the contents of F and P_2O_5 in PG were reduced by 98.33% and 67.35%, the removal rates of MgO, SiO₂, Al₂O₃, Fe₂O₃, and organic matter were 80%, 79.4%, 80.74%, 78.33%, and 89.66%, respectively. The soluble fluorine and soluble phosphorus were less than 0.1%, and the grade of gypsum was increased to 95.61%. Finally, the new PG yield of the overall optimization process is 82.15%, the gypsum recovery rate is 95.33%, and the whiteness was increased to 70.8%. This work provides a facile method to solve the problem of resource utilization of PG.

Table 2. Composition analysis of the solid product

Compound	F(soluble)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅ (soluble)	SO ₃	K ₂ O	CaO	Fe ₂ O ₃	TiO ₂	ZnO	SrO	LOI(OM*)
PG tailings (%)	3.36 (-)	0.24	0.18	3.23	45.92	0.32 (-)	27.77	2.08	14.25	2.12	0.39	0.01	0.03	13.05(4.26)
Old PG (%)	1.2 (1.07)	0.33	0.15	1.35	11.70	0.98 (0.72)	49.76	1.03	32.63	0.6	0.18	0.01	0.05	18.9(1.45)
Floated PG (%)	0.41 (0.14)	0.25	0.09	0.34	1.52	0.38 (0.11)	55.57	0.42	40.24	0.11	0.11	0.01	0.06	20.25(0.12)
New PG (%)	0.02 (0.01)	0.11	0.03	0.26	2.41	0.32 (0.04)	56.9	0.15	38.71	0.13	0.12	0.01	0.05	20.30(0.15)

OM*: organic matter

3.5.2. FTIR analysis

To further determine the phase components and change in solid products, the FTIR of the solid products was detected, shown in Fig. 7. In the FTIR spectra, the presence of water was confirmed by the characteristic transmission bands in the 3750-3250 cm⁻¹ and 1750-1500 cm⁻¹ regions. The bands in the 1250-1000 cm⁻¹ and 750-500 cm⁻¹ regions were assigned as ν_3 SO₄²⁻ and ν_4 SO₄²⁻. Therefore, it was further verified that there are gypsum dihydrate components in solid products. The bond around 480 cm⁻¹ is attributed to the asymmetrical bending vibration of Si-O-Si, the bond around 694 cm⁻¹ is assigned to the asymmetrical bending vibration of Si-O and the peaks at 790 cm⁻¹ and 1122 cm⁻¹ correspond to the symmetrical and asymmetrical vibration of Si-O, which indicates a significant decrease in silicon content in gypsum products after flotation and purification.

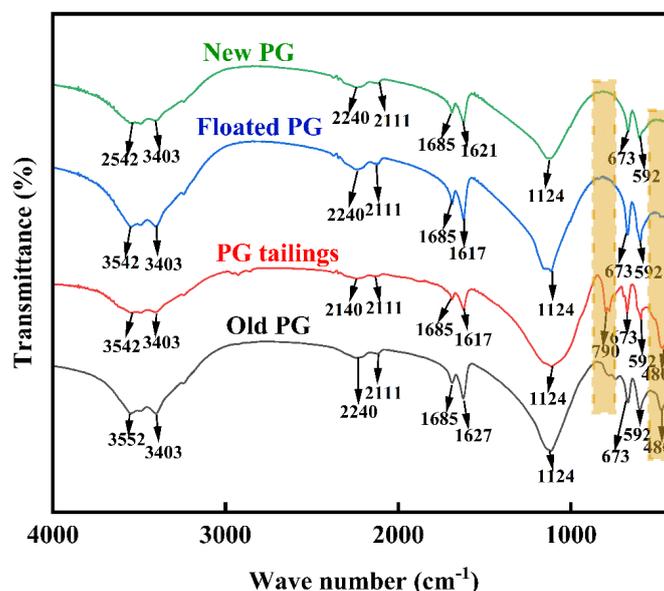


Fig. 7. The FTIR spectra of solid products

3.5.3. SEM image analysis

In order to visually analyze the difference of gypsum before and after purification, SEM analysis and comparison were conducted on the solid products, and the results were shown in Fig. 8. Fig. 8 (a) shows the SEM image of the old PG. It can be observed that the PG is predominantly present in the form of rhombic plates, with a minor occurrence of long strips. Some PG end faces exhibited incomplete crystallization, with the presence of flaky faults and a random distribution of fracture locations. Fig. 8 (b) shows the morphology of PG tailings. It can be seen that there were some gypsum crystals, which is caused by the inevitable entrainment phenomenon in the floc flotation separation process. Compared

with old PG, the particles in Fig. 8 (c) become smaller and cleaner with a clear contour, contributing to the removal of the impurities from the surface of the floated PG. Fig. 8 (d) shows the SEM of new PG, whose overall gypsum grain is more regular and cleaner than floated PG, indicating higher purity. The new process has resulted in the removal of impurities from PG, while maintaining the crystal structure.

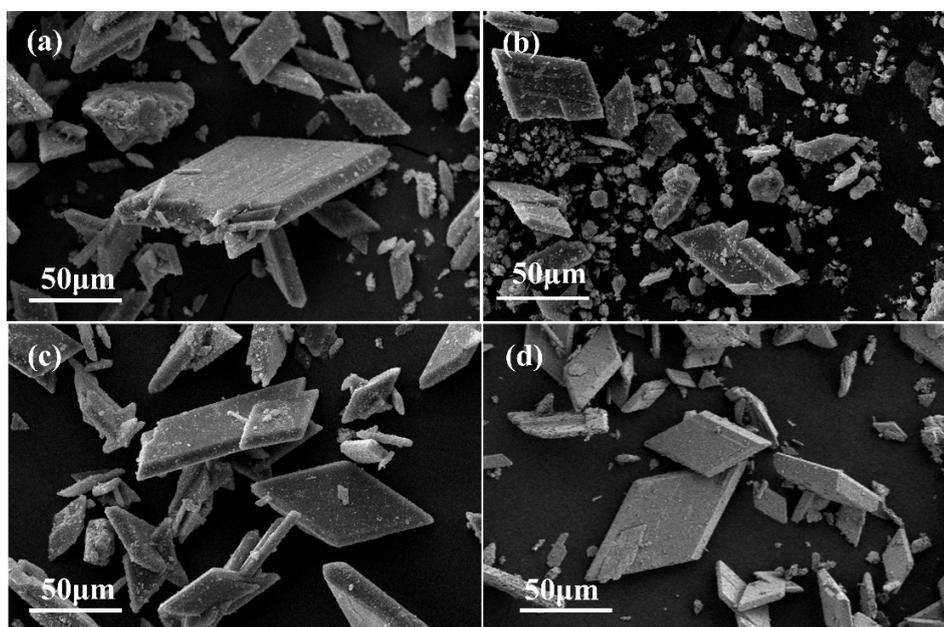


Fig. 8. SEM images of (a) old PG, (b) PG tailings, (c) floated PG, and (d) new PG

3.6. Analysis of phosphoric acid

The quality analysis of the liquid phase produced in the new process is shown in Table 3. The data demonstrated that the phosphorus content of the crude phosphoric acid had increased by approximately 1%, indicating that the recovery rate of phosphorus had been enhanced and a greater quantity of phosphorus had been introduced into the solution. This is due to the fact that the floc surface was hydrophobic, which made it difficult for the hydrophilic phosphoric acid to adsorb and retain on the floc. This resulted in a low phosphoric acid entrainment in the floc and a higher phosphorus recovery. The phosphoric acid density was proportional to the phosphorus content, which was slightly increased. In WPPA, the solid impurity was an important indicator that affects the quality of phosphoric acid. The high solid impurity would cause scaling in phosphoric acid storage tanks and pipelines in the future, and affect the quality of phosphoric acid. Through the optimization, the solid impurity of crude phosphoric acid was reduced by 95.31%, greatly improving the quality of phosphoric acid. The density increases of the phosphoric acid liquid after flotation further proved that the purity of phosphoric acid has been improved. The smaller solid impurity with higher P_2O_5 content would greatly improve the quality of the final phosphoric acid in the next process.

Table 3. Composition analysis results of wet phosphoric acid

Project	Phosphoric acid (Calculated by P_2O_5) $\omega/\%$	Density(g/cm^3)	Solid impurity $\omega/\%$
New process	32.64	1.74	0.03
Old process	31.61	1.62	0.64

3.7. Theoretical model for floc flotation and acid cleaning

In the floc flotation of PG, a single collector often did little work. The combination of collector and polymer flocculant has better flocculation and floc flotation selectivity for organic matter and siliceous fine particles, and acid cleaning can significantly reduce the pollution components of PG. The proposed principle is shown in Fig. 9. Following the addition of the flocculant, flocs are formed between the

flocculant, organic matter and siliceous fine particles due to the combined effects of adsorption bridging, net trapping and sweeping. After adding the collector, the self-assembly adsorption of the collector and floc makes the surface of the floc hydrophobic, which strengthens the hydrophobic effect between flocs. Finally, driven by the floc flotation bubble, it floats up to the foam layer to achieve selective separation from gypsum. The pollution component phosphorus in PG mainly exists in the form of soluble phosphorus, insoluble phosphorus, and eutectic phosphorus. The eutectic phosphorus is in the gypsum phase, which is difficult to dissolve unless the crystal phase changes, having low environmental pollution. The other phosphorus components, soluble or insoluble phosphorus, would dissolve or be decomposed, which can be washed by water and diluted sulfuric acid. Meanwhile, the pollution component fluorine also mainly exists in the form of soluble fluorine and insoluble fluorine on the surface of gypsum. By acid cleaning, all acid-soluble components on the surface of the PG will be dissolved and leached, resulting in a significant reduction in the pollution components of PG.

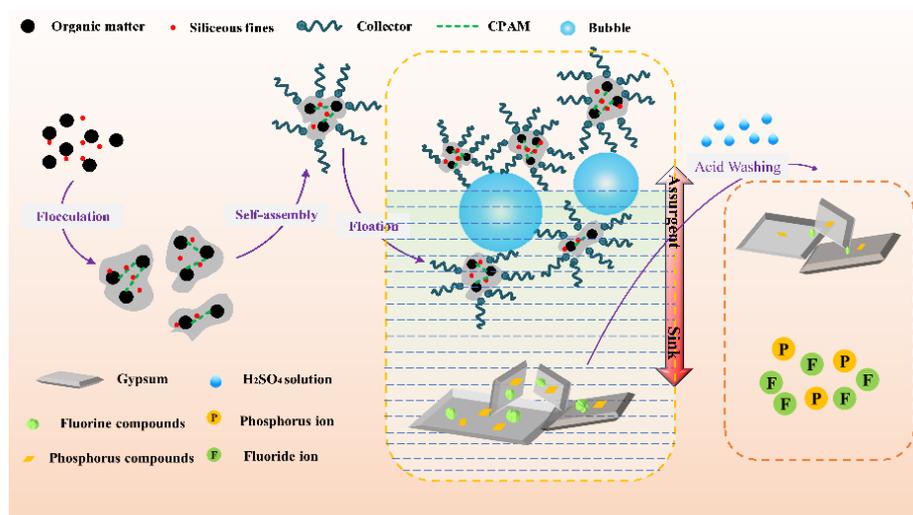


Fig. 9. Schematic depicting the role of new WPPA

4. Conclusions

In this work, a new WPPA was proposed, which not only improved the quality of the obtained phosphoric acid but also greatly reduced the impurities in PG. The new WPPA kept the old process unchanged by only adding flotation and acid cleaning procedures after the hydrolysis decomposition reaction. The parameters were determined as follows: floc flotation temperature was 65 °C, flocculant dosage was 180 g/Mg, collector dosage was 1.08 kg/Mg, and flushing sulfuric acid concentration was 20%. The obtained new PG reached the quality standard for first-class gypsum, transferring the waste solid in the original WPPA into a valuable gypsum resource. The study of the mechanism showed that the flotation reagents can effectively separate delicate organic matter and siliceous substances from PG, and harmful components in PG can be further removed by 20% H₂SO₄ washing. By optimizing wet-process phosphoric acid, we will obtain high-quality gypsum products and phosphoric acid, which would be an advanced technology for improving the quality and efficiency of WPPA plants and realizing cleaner production.

Acknowledgments

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Supplementary material

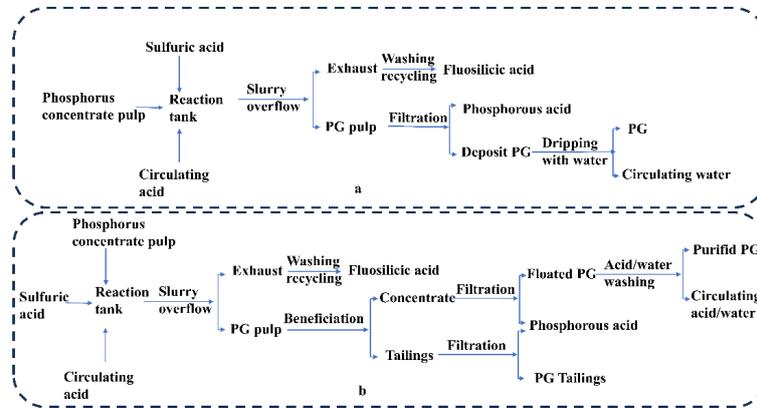


Fig. S1. Flow scheme of the traditional WPPA process (a) and the new strategy for WPPA (b)

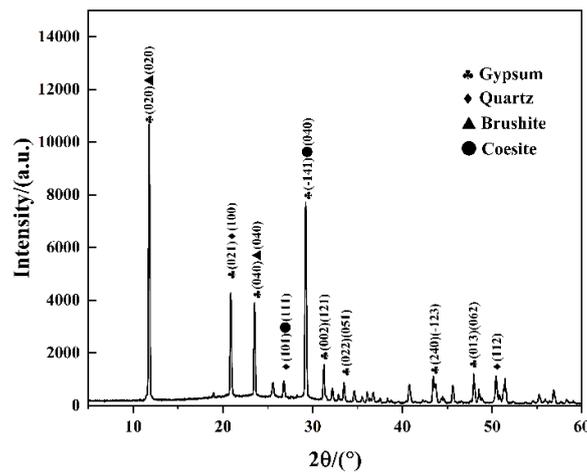


Fig. S2. The XRD of old PG

Table S1. Phosphogypsum index

Project	Index		
	First-class	Second-class	Three-class
Attached water (H ₂ O) (wet basis) / %	≤15	≤20	≤25
Calcium sulfate dihydrate (CaSO ₄ ·2H ₂ O) (dry basis) / %	≥90	≥80	≥65
Water-soluble phosphorus pentoxide (P ₂ O ₅) (dry basis) / %	≤0.20	≤0.30	≤0.50
Water-soluble fluoride ion (F ⁻) (dry basis) / %	≤0.10	≤0.20	≤0.30
Water-soluble magnesium oxide (MgO) (dry basis) / %	≤0.10	≤0.30	-
Water-soluble sodium oxide (Na ₂ O) (dry basis) / %	≤0.06	≤0.10	-
Chloride ion (Cl ⁻) (dry basis) / %	≤0.02	≤0.04	-

Table S2. Multi-element analysis results of old PG

Compound	F(soluble)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅ (soluble)	SO ₃
Content (%)	1.2(1.07)	0.33	0.15	1.35	11.70	0.98(0.72)	49.76
Compound	K ₂ O	CaO	Fe ₂ O ₃	TiO ₂	ZnO	SrO	LOI(OM*)
Content (%)	1.03	32.63	0.6	0.18	0.01	0.05	18.9(1.45)

Table S3. Composition analysis results of old process wet phosphoric acid

Project	Phosphoric acid (Calculated by P ₂ O ₅) ω/%	Density(g/mL)	Solid impurity ω/%
Old process	31.61	1.62	0.64