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A novel method for purification of phosphogypsum

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Abstract: Phosphogypsum is an industrial solid waste from the phosphate fertilizer industry. At present, the accumulation of phosphogypsum has caused very serious economic and environmental problems. A large scale of phosphogypsum is consumed in the building field. The characteristics of whiteness and phosphorus content are important factors affecting the use of phosphogypsum as a building material. In this study, soluble phosphorus and fluorine were removed by adding lime, and flotation was employed to purify phosphogypsum. A large amount of organic matter and fine slime in the phosphogypsum were removed by reverse flotation, and gypsum was floated by positive flotation. Through the flotation closed-circuit experiment, the whiteness of phosphogypsum was increased from 31.5 to 58.4, the percentage of total phosphorus in gypsum (P_2O_5) was reduced from 1.78 to 0.89, the grade of calcium sulphate dihydrate was 96.6%, the recovery of concentrate was 74.1%. After removing impurities, the phosphogypsum concentrate reached the first grade national standard of the phosphogypsum building materials in China. The method is cheap and practical, and can be used as an important method for pretreatment of phosphogypsum.

Keywords: phosphogypsum, purification, phosphorus, fluorine, building materials

1. Introduction

Phosphorus is an indispensable fertilizer element in agriculture (Ciceri and Allanore, 2019), which is mainly obtained by wet sulfuric acid leaching of apatite. However, in addition to phosphoric acid, a large amount of phosphogypsum (PG) is produced as an industrial by-product (Silva et al., 2010). The production of one ton of phosphoric acid will produce 4.5-5.5 tons of PG (Yang et al., 2013; Contreras et al., 2018). So far, the storage of PG in China has exceeded 400 million tons, and the global storage has exceeded 6 billion tons (Ma et al., 2020; Degirmenci, 2008). For a long time, PG can only be piled up at random, which occupies a large amount of land. The pollutants in the PG are easy to seep out, which will pollute the water and the surrounding environment (Tayibi et al., 2009; Canovas et al., 2018). In addition, it can form dust and cause very serious environmental problems in the local area (Xue et al., 2019; Xu et al., 2019; Hartley et al., 2013). At present, China has established a system for determining the output by consumption. This has brought tremendous pressure to phosphorus chemical companies and also determined the survival of phosphorus chemical companies (Xu et al., 2019).

Natural gypsum is an important non-metallic mineral, which can be used in cement retarder, ceramics, gypsum plaster, gypsum wallboard, gypsum mortar and other building materials industry (Islam et al., 2017; Schug et al., 2017; Engbrecht et al., 2016; Rashad et al., 2017). A large amount of gypsum resources is needed every year, among which the building materials industry is the largest

consumer of gypsum. The main components of phosphogypsum and natural gypsum are calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The content of calcium sulfate dihydrate in phosphogypsum exceeds 85% (Alcordo et al., 1993), which is usually higher than natural gypsum. The application of PG in building materials industry not only reduces the mining of gypsum ore, but also eliminates a large amount of the industrial waste of phosphorus chemical enterprises (Mashifana 2019; Jiang et al., 2018). This not only reduces the environmental pollution of PG, but also converts waste into wealth, becoming an inevitable choice for the sustainable development of the phosphate fertilizer industry. However, PG contains a large amount of impurities, mainly organic matter, soluble phosphorus, soluble fluorine, eutectic phosphorus, eutectic fluorine, quartz and so on (Ding et al., 2019). A large number of studies have revealed that soluble phosphorus, soluble fluorine, eutectic phosphorus, and eutectic fluorine will affect the use of PG as building materials (Huang et al., 2019). Soluble phosphorus and soluble fluorine will increase the initial setting time of cement. Besides, the presence of phosphorus and fluorine in building materials will also cause water absorption and frosting of building materials. In addition, the presence of organic matter and slime will result in low whiteness of PG. These reasons have seriously affected the use of PG in the building materials industry (Singh et al., 1996; Singh, 2005). For a long time, the majority of science and technology workers have done a lot of researches on the purification of PG (Singh et al., 1993), which mainly focus on the following aspects. The first is the water washing method, which can remove a large amount of soluble phosphorus and fluorine. However, due to secondary wastewater and high investment costs, this method is difficult to apply in the industrial field. The second is the traditional flotation method, which can remove organic matter suspended in PG slurry naturally without adding flotation agents, but cannot remove phosphorus and fluorine. Besides, this method is slow and inefficient. Another is the precipitation method. Lime is added to the PG. The soluble phosphorus and fluorine in the lime and PG react to form insoluble phosphorus and fluorine, which reduces the influence of soluble phosphorus and fluorine on the building materials. However, after a long time, insoluble phosphorus and fluorine will dissolve out, which cannot fundamentally reduce the influence of phosphorus and fluorine on PG (Singh, 2002; Reijnders, 2007).

After reviewing the deficiency of previous studies, soluble phosphorus, fluorine were precipitated by lime firstly. Organic matter and slime in PG were floated out by the reverse flotation method, and the fine particles of phosphorus and fluorine minerals were also enriched and removed. Then, gypsum is positively floated by adding an amine collector, and a large amount of phosphorus-containing high minerals enter the flotation tailings. Through positive and negative flotation, the whiteness and purity of PG are improved, and the content of fluorine and phosphorus is reduced. This research has important guiding significance for the harmlessness and resource utilization of PG.

2. Experimental

2.1. Samples and reagents

The sample was purchased Hongda Phosphorus Chemical Co., Ltd., Deyang, China. The results of multi-element analysis of the samples are shown in table 1. It shows that Ca and S were the main element components in the PG, and the main impurity elements was Si. The total phosphorus (P_2O_5) content in the sample was 1.78%. The phosphorus content was high and needed to be removed. The F content in this sample was low. Through ion chromatography analysis, the soluble phosphorus content in the PG sample was 0.40%. After testing by the whiteness meter, the whiteness of the raw sample was only 31.3. Besides, The content of calcium sulphate dihydrate in PG ore was 86.5% by the determination of crystal water firing loss. The XRD analysis results of PG are shown in Fig. 1. The results show that the main mineral in the PG is calcium sulphate dihydrate and contains a small amount of unreacted phosphorite ($\text{CaPO}_3(\text{OH})_x \cdot 2\text{H}_2\text{O}$).

Dodecyltrimethyl ammonium chloride (DTAC) used in the experiment was of analytical grade and was obtained from Nanjing Robiot Co., Ltd, Nanjing. In addition, Pine oil used in the experiment is industrial grade.

2.2. Precipitation test of soluble phosphorus and fluorine

5 g phosphogypsum was added into a beaker with 25 mL water, then lime was incorporated with a certain mass ratio to phosphogypsum and the mixture was stirred for 5 minutes. Subsequently, the

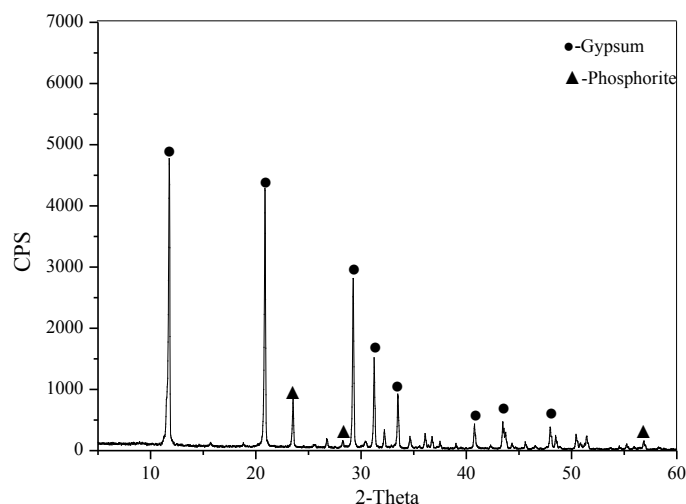


Fig. 1. XRD pattern of PG raw ore

Table 1. Elemental analysis results of PG raw ore

Compound	SO ₃	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	SrO
Content (%)	49.03	39.47	3.68	2.59	1.95	1.78	0.69
Compound	K ₂ O	TiO ₂	F	BaO	MgO	Y ₂ O ₃	
Content (%)	0.29	0.27	0.06	0.07	0.02	0.02	

mixture was filtered, and then the filtrate was transferred into a 100 mL volumetric flask. Then, its volume was determined by deionized water. Finally, the concentration of soluble phosphorus and fluorine in the filtrate was analyzed and recorded.

2.3. Flotation tests

The flotation tests were carried out on a 1 L XFD type flotation machine, and 200 g samples were tested. Local tap water was used in flotation tests. First, add 2 grams of lime (1%) to the slurry, stir for 5 minutes to precipitate soluble phosphorus and fluorine, then add pine oil, remove organic matter and slime in PG by reverse flotation, and finally add DTAC to floating gypsum for concentration. The samples were filtered, dried at 40°C, weighed, and the recovery was calculated. The whiteness of the sample were investigated by the SBDY-1P whiteness meter, Shanghai Yuefeng Instrument Co., Ltd. The content of total phosphorus in the sample was measured using wavelength dispersive X-ray fluorescence spectrometer (XRF), and the soluble phosphorus and fluorine in the sample were determined by ion chromatographic analyzer.

2.4. Gypsum purity test

The purity of calcium sulphate dihydrate in PG was determined by the content of crystallized water in gypsum. The mass fraction of calcium sulphate dihydrate (G) in sample was calculated according to formula (1)

$$G = 4.7785 \times H \quad (1)$$

where G is the purity of calcium sulphate dihydrate, %, 4.7785 is coefficient of calcium sulfate dihydrate content converted from crystal water content, which is equal to the molecular weight of calcium sulfate dihydrate divided by the molecular weight of two water molecules. H represents crystal water content, %.

2.5. SEM analysis

The raw ore and concentrate samples were analyzed by SEM. The testing equipment is sigma300 scanning electron microscope produced by Zeiss in Germany.

3. Results and discussion

3.1. Results of soluble phosphorus and fluorine precipitation

The influence of lime addition (add in mass ratio with PG) on the concentration of soluble phosphorus and fluorine in PG was investigated and the corresponding results are shown in Fig. 2. The soluble phosphorus and fluorine in PG can be solidified by adding lime. When the addition amount was 1% of the mass of PG, the content of soluble phosphorus and fluorine was 0.71 mg/L and 0.041 mg/L, respectively, which were far lower than 0.2% and 0.1% of soluble phosphorus and fluorine required by the national standard for phosphogypsum first-class products.

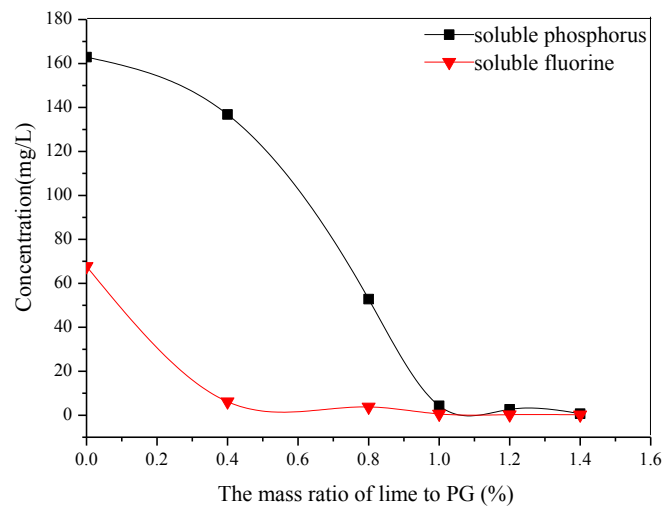


Fig. 2. Effect of lime content on the concentration of soluble phosphorus and fluorine in PG

3.2. Flotation removal test of organic matter and fine slime

PG contains a lot of slime and organic matter, which leads to the low whiteness of PG and the accumulation of phosphate minerals in the fine slime. It is hydrophobic and can be removed by adding a small amount of foaming agent. Therefore, the flotation method was employed to float out organic matter and slime. The use of frother is a common method of flotation desilting. Pine oil is one of the most commonly used foaming agents with relatively low cost and good foaming performance (Liu, et al., 2020). The effect of pine oil dosage on removal of slime and organic matter from PG was investigated in this section. The flow chart of of pine oil dosage test is shown in Fig. 3. The results of pine oil dosage test is shown in Fig. 4.

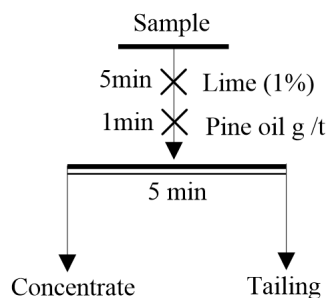


Fig. 3. Flow chart of of pine oil dosage test

Fig. 4 (a) shows that with the increase of pine oil dosage, the recovery of gypsum concentrate reduced, the recovery of organic matter and slime in the tailings increased and the purity of gypsum increased, indicating that the increase of pine oil dosage was beneficial to the removal of slime and organic matter. However, if the amount of foaming agent was too large, gypsum would also be entrained and float, and the recovery of gypsum would decrease. Fig. 4(b) shows that as the dosage of pine oil increases, the total phosphorus content in the concentrate decreases and the whiteness of gypsum increases, indicating that phosphorus is abundant in slime and organic matter. Not only the organic matter and

slime removed, but also the phosphorus content in the gypsum concentrate also reduced. When the dosage of pine oil reached 250 g/t, with the continuous increase of pine oil, the recovery of impurities, the whiteness and purity of gypsum concentrate stopped increasing, and the total P_2O_5 concentration in gypsum concentrate was no longer decreased. Due to the increased cost of pine oil dosage, the pine oil dosage was set at 250 g/t in subsequent tests.

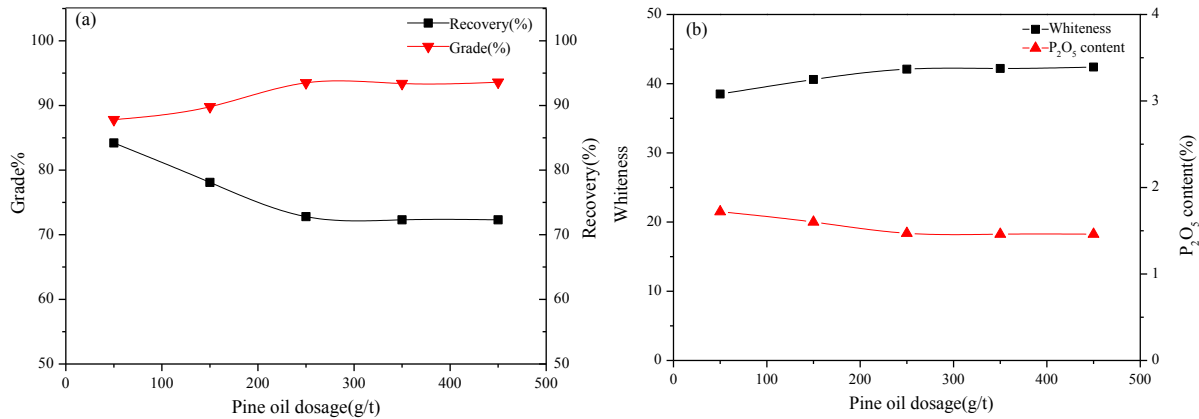


Fig. 4. Results of pine oil dosage test

3.3. Collector dosage test

After removing impurities such as slime and organic matter, there were still some impurity minerals in the PG, which were mainly coarse-grained phosphorite. These impurities will affect the whiteness of PG, and phosphorus will be enriched in these impurities. Therefore, it is necessary to separate these impurities from calcium sulphate dihydrate. The surface of calcium sulphate dihydrate was negatively charged in wide pH range, and cationic collector has a good ability to collect it (Lu et al., 2008; Raii et al., 2014). Quaternary ammonium salts are a common cationic collectors used in the flotation of various negatively charged minerals (Hu et al., 2012; Wang and Ren, 2005; Jiang et al., 2019). DTAC is one of the most representative quaternary ammonium salt collector (Tian et al., 2017; Rahimi et al., 2017). However, it has not been reported on gypsum flotation. Therefore, the commonly used cationic collector dodecyltrimethyl ammonium chloride (DTAC) was investigated for calcium sulphate dihydrate flotation. The effect of DTAC dosage on the purity and whiteness of gypsum was studied. The experimental process is shown in Fig. 5, and the result of the flotation concentrate index is shown in Fig. 6.

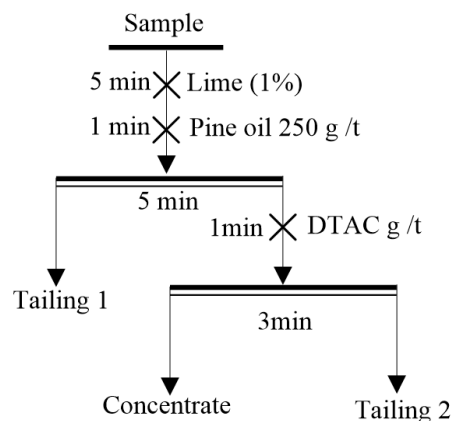


Fig. 5. Flow chart of DTAC dosage tests

From the results of DTAC dosage, it can be seen from Fig. 6 that with the increase of DTAC dosage, the recovery and total P_2O_5 content of concentrates gradually increased. When the DTAC dosage reaches 100 g/t and continued to increase, the recovery of concentrate increased slightly, while the total P_2O_5 grade of concentrate increased significantly. On the contrary, with the increase of DTAC dosage, the grade and whiteness of calcium sulphate dihydrate gradually decreased. This is mainly due to the

increase in reagent dosage, which leads to an increase in the recovery rate of the concentrate and the easy inclusion of other impurities. Comprehensively considering the factors such as the purity, recovery, whiteness and phosphorus content of PG, the dosage of DTAC was set at 100 g/t.

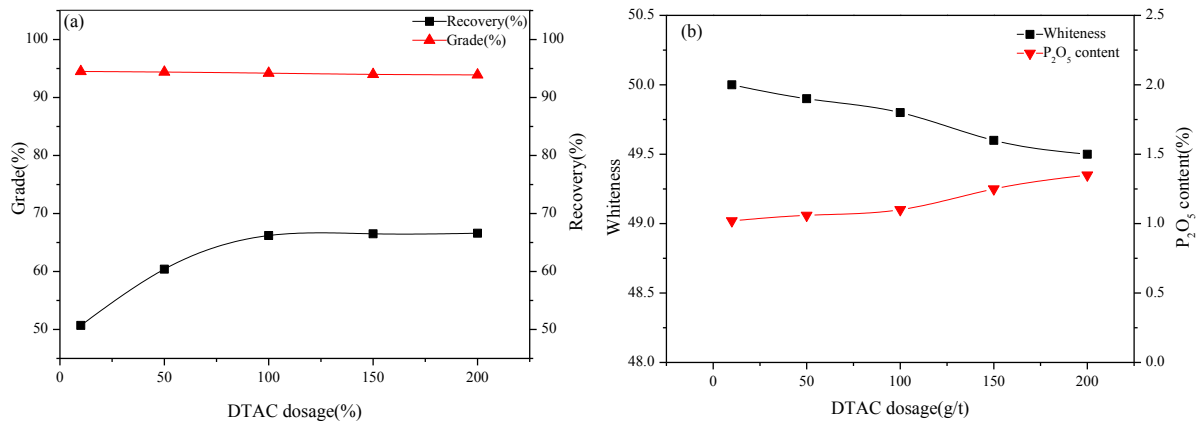


Fig. 6. Results of DTAC dosage test

3.4. Closed circuit test of PG flotation

After the reverse flotation, the positive flotation of DTAC to PG was carried out. Good flotation indexes could be obtained by the closed-circuit process of "one rougher, two cleaners and one scavenger". The flow chart is shown in Fig. 7, and the results are shown in table 2.

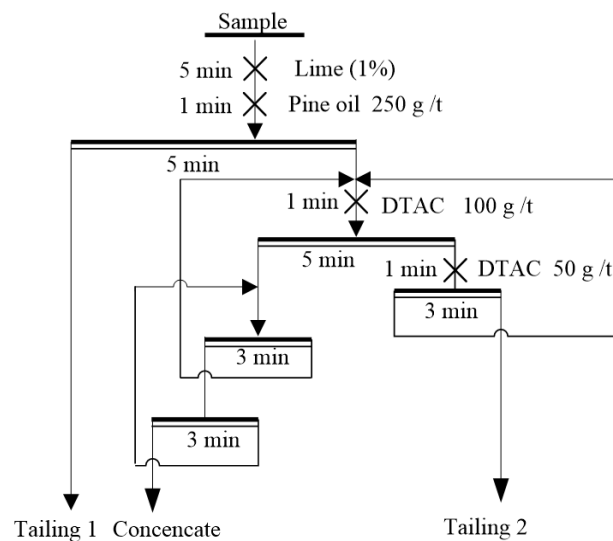


Fig. 7. Flow chart of closed circuit flotation tests for PG

Table 2. Results of closed-circuit tests for PG

Index Product	Grade (%)	Recovery%	Whiteness	Total P ₂ O ₅ %
Concentrate	96.6	74.1	58.2	0.89
Tailing 1	66.68	21.4	34.2	2.73
Tailing 2	66.4	4.5	33.2	7.30
Raw ore	86.5	100	33.8	1.78

After open-circuit reverse flotation and the closed-circuit "one rougher, two cleaners and one scavenger" process, the grade of gypsum was 96.6%. After purification, the whiteness of PG reached 58.2, which was 24.4 higher than that of raw ore. The total phosphorus content (P₂O₅) in PG also decreased from 1.78% to 0.89%. The soluble phosphorus and fluorine in the slurry have been

precipitated and the beneficiation wastewater can be recovered. The flotation concentrate meets the requirements of Chinese national standard (GB/T 23456-2018) for PG grade products.

3.5. SEM analysis results

Scanning electron microscopy of the raw ores and concentrates are shown in Figs. 8 (a) and (b), respectively. It can be seen from the figure that the PG in the raw ore showed a state of aggregation, the particles adhered to each other, and the surface of the gypsum crystals was covered with fine mineral particles. After separation, the gypsum particles in the concentrate were dispersed, the fine slime on the surface of the particles was removed, and the surface of the gypsum crystals was smooth and clean, which proved that the flotation method can effectively removed impurity minerals in PG and improved the purity of gypsum.

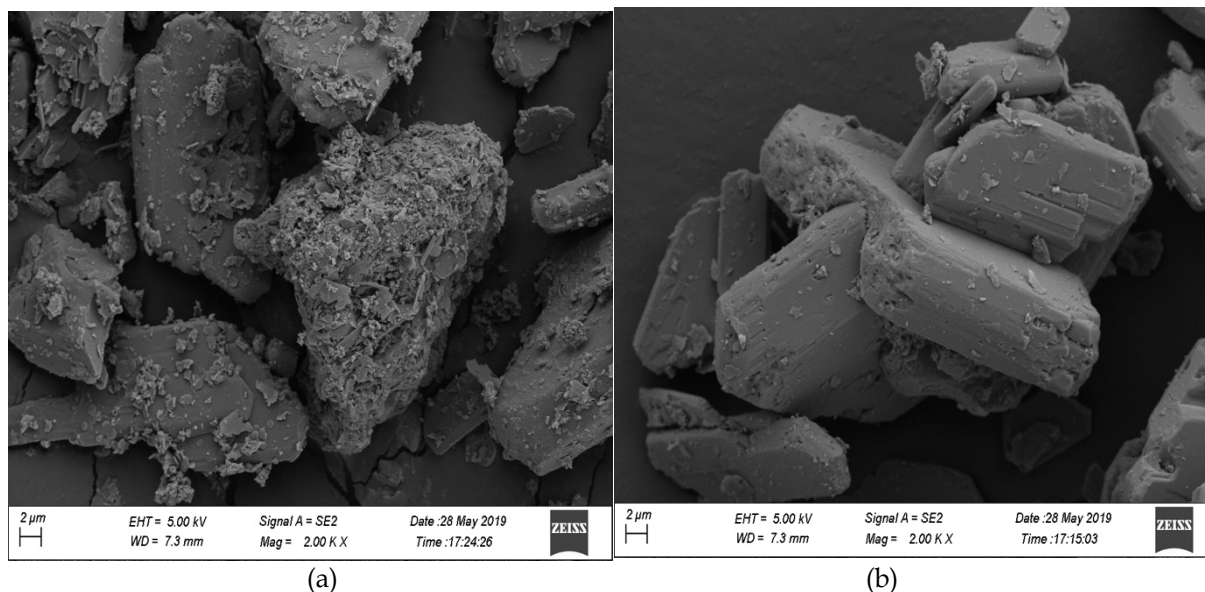


Fig. 8. SEM of raw ore (a) and concentrate (b)

4. Conclusions

Lime could precipitate soluble phosphorus and fluorine in phosphogypsum. Organic matter and easy-to-float slime in PG can be removed by desliming flotation. In addition, the whiteness and purity of PG are also greatly improved. Phosphorus in the removed slime was enriched and the phosphorus content in the gypsum concentrate was reduced. After open-circuit reverse flotation of desliming, DTAC was used as the collector, and the closed-loop positive flotation process of "one rougher, two cleaners, and one scavenger" was adopted. The whiteness of the PG concentrate reached 58 and the purity of calcium sulphate dihydrate reached 96.6%. The flotation concentrate meets the requirements of the national standard GB/T 23456-2018.

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