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## Research of nanobubbles enhanced reverse anionic flotation of a mid-low grade phosphate ore

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**Abstract:** The reverse anionic flotation is commonly used to upgrade the mid-low grade phosphate ore in China. The mineral characterization of raw ore shows that carbonate and phosphate minerals combined with fine intergrowth, difficulty in upgrading. Flotation using nanobubbles (NBs) can significantly enhance the flotation efficiency of fine particles of minerals. To research the effect of NBs on the flotation process of this phosphate ore, two flotation tests with and without NBs were compared. The results show that the MgO removal had an increment of 10% in the case of NBs flotation versus conventional flotation in the approximate grade and recovery of P<sub>2</sub>O<sub>5</sub>. The foam product of NBs flotation had smaller dimensions than the conventional flotation. NBs enhanced the contact angle on dolomite surface from 45.8 ° to 64.5 °, and increases the d<sub>50</sub> of dolomite from 20.49 μm to 30.43 μm.

**Keywords:** nanobubbles, reverse anionic flotation, phosphate ore, dolomite, particle aggregation

### 1. Introduction

Phosphorus is an important element in the ecosystem, and it maintains the growth of animals and plants. Phosphate ore is the raw material for phosphorous chemical industry. China has the second-largest phosphate reserve in the world (Survey, 2021); its phosphate ore deposits are mainly attributed to marine sedimentary origin (Abouzeid, 2008), and more than 90% are mid-low grade phosphate ore which needs processing and upgrading. Froth flotation is a common method for the beneficiation of low-grade sedimentary phosphate ore (Ruan et al., 2019). More than 50% of phosphate products of the world are produced by flotation (Sis and Chander, 2003). The useful mineral of phosphate ore is apatite, and the common gangues are dolomite, calcite, quartz (Li et al., 2017), clay minerals, etc (Hoang et al., 2018). Another character of Chinese phosphate ore is high magnesium content (Huang et al., 2014). Dolomite is the main source of magnesium in phosphate ore. The wet phosphoric process for the phosphate concentrate must have a content of MgO less than 1% (Sis and Chander, 2003). The common flotation schemes can be classified into direct flotation, reverse flotation, direct-reverse flotation, and double-reverse flotation. Apatite and dolomite both belong to calcium-containing minerals which have Ca<sup>2+</sup> on the surface (Xie and Zhang, 2021). Therefore, dolomite and apatite have similar physicochemical properties, which resulted in difficulty of separation between dolomite and apatite. The reverse flotation process is more suitable for dolomite removal from phosphate ore (Huang et al., 2021). In the flotation of dolomite from phosphate ore, fatty acid salts, especially sodium oleate, are often used as collector while sulfuric acid or phosphoric acid was used as depressant and regulator. There are also researches using acidic wastewater produced by phosphorus chemical process (mainly composed of sulfuric acid and phosphoric acid mixture) as regulator (Xu et al., 2008), and it not only saves costs but also reduces environmental pressure while obtaining a better flotation index. However, for mid-low grade

phosphate ore, carbonate and phosphate minerals combined with fine intergrowth (Hoang et al., 2018). It has some properties which are unfavorable to flotation, for example, the comminution and the conditioning would produce large amounts of slimes, the micron-sized pores of the sedimentary phosphates increase the surface area of the particle, grinding to a very fine size to liberate the dolomite inclusions. Those properties reduce the flotation rate and recovery rate (Miettinen et al., 2010), decrease selectivity of reagents, increase the consumption of reagents, increase the entrainment of hydrophilic particles (Wang et al., 2015).

Recently, nanobubbles (NBs), the diameter  $< 1 \mu\text{m}$ , have become a research hotspot. Although the stability of NBs has not been explained, NBs are being assessed for application to mineral separations using flotation (Alheshibri et al., 2016). Flotation in the presence of NBs shows better results than conventional flotation, especially while the particles are fine (Sobhy and Tao, 2013; Tao and Sobhy, 2019; Lei et al., 2020; Olszok et al., 2020). It has been reported that the very small diameter of NBs increases the probability of collision between particles and bubbles (Calgaroto et al., 2014); NBs can be used as secondary collectors to reduce collector consumption (Tao et al., 2008; FAN et al., 2010); NBs can connect to form the gas bridge and attractive capillary force, which promotes the aggregation of hydrophobic particles (Knüpfer et al., 2017). To determine the effects of NBs on flotation index of coarse and fine particles. Nazari et al. (Nazari et al., 2018) separated coarse pure quartz ( $-425+106 \mu\text{m}$ ) with NBs and increased recovery by 14% compared with flotation without NBs; Calgaroto et al. (Calgaroto et al., 2015) found that in the presence of NBs, fine and ultrafine quartz flotation recovery increased by 20-30%; Fan et al. (Fan et al., 2013) proposed that NBs extend the lower and upper particle size limits for coal flotation. The enhanced flotation effect of NBs have also been reported in chalcopyrite (Ahmadi et al., 2014), coal (Chang et al., 2020; Li et al., 2020) and muscovite (Zhou et al., 2019). But, Chipakwe et al. (Chipakwe et al., 2021) found the NBs generated with surfactants could cause a decrease in grade, because of the increased entrainment rate.

However, over the past decade, most research in NBs enhanced flotation has mainly emphasized of direct flotation, and the study of NBs on improving reverse flotation performance is rarely reported. In this study, two flotation tests, with or without NBs, were used to carry out comparative tests under different operating conditions (grinding fineness, acid type, acid dosage, and collector dosage) in a mechanical flotation system. To investigate the effect of NBs on reverse anionic flotation of mid-low grade phosphate ore.

## 2. Materials and methods

### 2.1. Phosphate ore

Calcium-magnesium phosphate ore was taken from a sedimentary phosphate deposit in Guizhou province, China. It was broken to  $-2 \text{ mm}$  and preserved as raw ore sample. The mineral characteristics was analyzed by X-ray diffraction (X' Pert PRO, Netherlands PANalytical), the XRD pattern was shown in Fig. 1. The main minerals are fluorapatite ( $\text{Ca}_5\text{F}(\text{PO}_4)_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), a small amount of

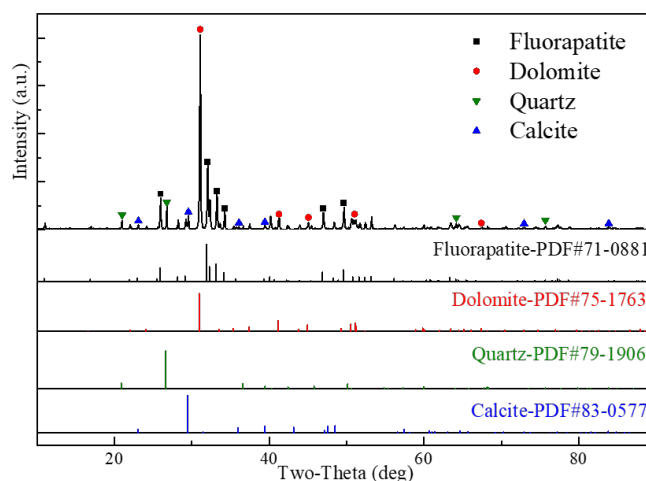


Fig. 1. XRD pattern of phosphate ore

Table 1. XRF results of phosphate ore

P <sub>2</sub> O <sub>5</sub> %	CaO%	MgO%	SiO <sub>2</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	Al <sub>2</sub> O <sub>3</sub> %	K <sub>2</sub> O%	TiO <sub>2</sub> %	Na <sub>2</sub> O%	L.O.I.%
24.05	43.62	6.62	4.22	0.51	1.11	0.11	0.03	0.11	19.66

L.O.I.: loss-on-ignition

quartz (SiO<sub>2</sub>) and calcite (CaCO<sub>3</sub>). The chemical composition of the sample was determined by X-ray fluorescence spectrometry (Axios mA×4KW, Netherlands PANalytical), the results are shown in Table 1. The grade of P<sub>2</sub>O<sub>5</sub> was 24.05%, and the content of MgO was 6.62%. Other impurities such as SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> were low.

Advanced Mineral Identification and Characterisation System (AMICS, AMICS-Mining/SIGMA 500, ZEISS/Bruker) was used to study on mineral characterization of the raw ore. The ore samples were crushed to -0.2 mm and then the particle samples were cold-mounted in a cylinder using epoxy resin. AMICS operates with a 20 kV acceleration voltage, high vacuum, and 9.42 mm working distance. As shown in Fig. 2(a)-(f), apart from existing in the form of liberated particles, apatite was also present in dolomite and quartz as a composite particle and the inclusions could be find. The particle size distributions of main minerals were measured, the results shown in Fig. 2(g) indicate that when particle grade is > 37.5 μm, the accumulated distribution rate of apatite and dolomite was 90.71% and 82.89%, respectively. Therefore, higher grinding fineness possibly was required to achieve complete liberation.

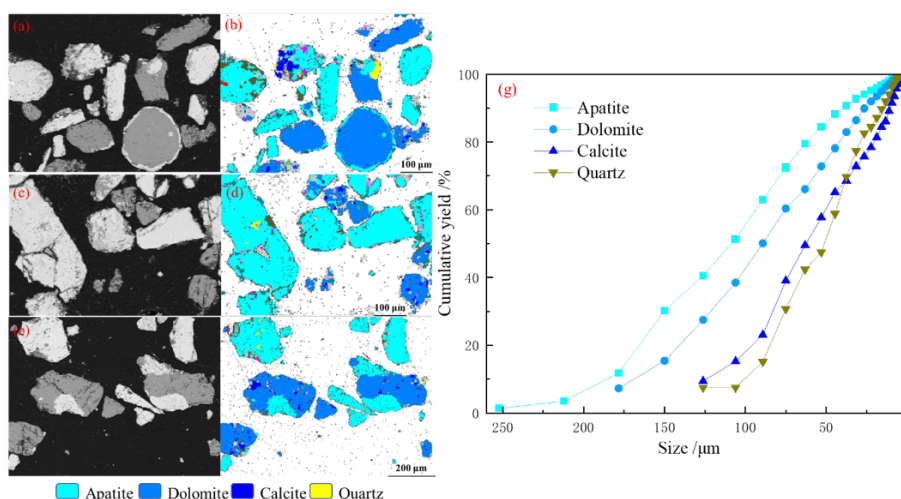


Fig. 2. (a)-(f) Association of main minerals. (g) Particle size distributions of major minerals

## 2.2. Generation and characterization of NBs water

NBs were produced by a micro-nano bubbles generator (ZJC-NM-200L, China Shanghai Zhongjing Environmental Protection Technology Co. LTD) which based on the principle of pressurized dissolved gas separate out bubbles. The generator is composed of a white transparent feeding tube, a steel micro-nano bubble nozzle and a machine body. The schematic diagram of the generator is shown in Fig. 3. Water or solution should be filled in the feeding tube before starting generator. Water and air are sucked into the machine body from the feeding tube and the air inlet respectively. The gas-liquid mixture in the generator rotates at high speed under pressure and then ejects from the specially designed micro-nano bubble nozzle. Large number of NBs generated by hydrodynamic cavitation at the nozzle. The nanobubble-containing solutions are released from the micro-nano bubble nozzle and are collected with a clean tank.

The micro-nano bubble generator cavitates 1000 cm<sup>3</sup> water for 6 min with 100 cm<sup>3</sup>/min air inlet rate, and 400 Kpa inlet pressure. After the completion of the machine, the photos were used to record the change process of the micro-nano bubble. Changes of nanobubble size with time were measured by Dynamic light scattering method (Zetasizer NanoZS 90, UK Malvern Instruments). Each size measurement was conducted at 25 C for 5 times, with the average recorded as the final reported data. The nanobubble size was measured at 25 °C when the refractive index of bubbles was set to be 1 and

the refractive index of water to be 1.33. Each size measurement was repeated 3 times, and the average was recorded as the final data. Tap-water was used in flotation test, Deionized water was used in pure mineral test.

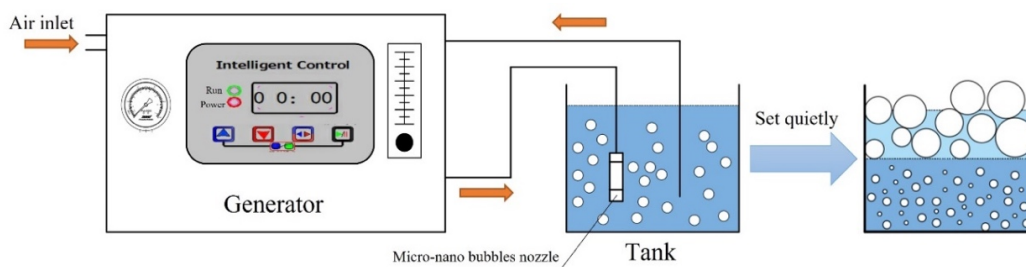


Fig. 3. Schematic of NBs generation process

### 2.3. Reagents

In this work, three acids (sulfuric acid, mixed acid and AW) were used to adjust pH value and inhibit apatite. Fatty acid salts are commonly used as collector in reverse anionic flotation, but it has problems such as poor selectivity, higher temperature requirement, large reagent consumption and susceptible to impurity ions in pulp (Sis and Chander, 2003). The compound use of surfactants has many synergistic advantages and improves the selectivity, water solubility and dispersion of pesticides (Ruan et al., 2019). GJBW, an anionic collector, is a fatty acid compound collector developed by our team, it has achieved good performance in flotation test (Ye et al., 2020). GJBW was prepared into 1% (w/w) solution for use.

Sulfuric acid ( $H_2SO_4$ ) with analytical grade  $\geq 95\%$  was supplied by JIANGCHUAN CHEMICAL INDUSTRY, China. A solution was prepared for application

Phosphoric acid ( $H_3PO_4$ ) with analytical grade = 85% was supplied by JIANGCHUAN CHEMICAL INDUSTRY, China.

Sulfuric acid and phosphoric acid were both configured into 20% (w/w) solution. Mixed acid was composed of phosphoric acid and sulfuric acid in 1:1 volume ratio.

AW was supplied by Wengfu (Group) Co., Ltd. China. It is a solution type regulator used in the flotation workshop of the company. AW is an acidic waste water which is produced by the production of wet-process phosphoric acid. The pH of this acidic waste water is 2.6~3, and its concentration of  $P_2O_5$  is 4500~6000 g/m<sup>3</sup>.

### 2.4. Flotation test

Conventional flotation (with Tap-water) and NBs flotation (with NBs-water) performed in a 0.75 L laboratory flotation machine (RK/FD II-0.75, China Wuhan Rock grinding equipment Manufacturing Co., LTD) to evaluate the feasibility of reverse anionic flotation of calcium-magnesium phosphate ore. 250 g of grinding ore sample was conditioned with Tap-water/NBs water in the flotation cell then the rotation speed of rotor was stirred to 1992 rpm. After stirring for 2 min, the pulp pH was adjusted to acidic for 1 min. Adding collector GJBW for 1 min. Open the inflator (0.1 m<sup>3</sup>/h) and the froth product was collected for a total time of 4 min. The concentrates and tailings were filtered, washed with water, dried, weighed. The content of  $P_2O_5$  and MgO in concentrates and tailings were analyzed by XRF to determine performance parameters such as concentrate  $P_2O_5$  recovery, grade and MgO removal efficiency.

### 2.5. Effect of NBs on surface and particle properties of minerals

The contact angle of minerals is usually used to characterize the hydrophobicity of mineral surfaces. In this work, contact angle was measured by a contact angle instrument (HARKE-SPCAX3, China Beijing Hake Test Instrument). Dolomite and apatite pure minerals were prepared from the raw ore, and the detailed preparation methods can be found in the study by WANG et al (Wang and Zhang, 2020). Contact angle with/without NBs was measured on the mineral surfaces by the sessile drop method;

Contact angle in the acidic condition was measured by captive bubble method. Each contact angle measurement was repeated 3 times, and the average was recorded as the final data.

Size distributions of foam products and pure minerals were measured through a laser particle analyzer (LS I3320, USA Bechman Coulter). The pure minerals were used to research the effect of NBs on particle dispersion/aggregation state. Mix 1g pure mineral and 199 mL deionized water/NBs water, add regulator AW and collector GJBW at lower stirring speed so that the pH value and collector concentration of pulp are consistent with the optimum conditions of flotation test, the pulp was stirred for 4 min at 600 rpm. The mineral suspension was measured by a laser particle analyzer and observed in an optical microscope (Olympus-BX51TRF, Japan Olympus corporation).

### 3. Results and discussion

#### 3.1. Preparation and characterization of NBs water

As shown in Fig. 4(a)-(f), the initial gas-liquid mixture water was milky because it contained a lot of micro-sized bubbles (Couto et al., 2009). Micro-sized bubbles gradually merged and broke as time went on, then the water was increasingly clear. It has been reported that NBs have excellent stability in water (Peng et al., 2015), the DLS technique was used to detect bubbles size in NBs water. Fig. 4(g) provides the average size of bubbles was 192 nm after 10 min deposition. The diameter of NBs produced by the same type of generator is reported to be between 100 and 200 nm (Xiao et al., 2018). Considering the possibility of shrinking, merging, bursting/collapsing after nanobubble generation, we increased the deposition time of NBs water and detect bubbles size. Although the NBs' average size increased gradually as deposition time (DT) went on, the average size of bubbles in solution was 581 nm after 48 h. No accepted theory to explain the long-time stability of bulk NBs, but it is not the focus of this work and will not be discussed too much (Alheshibri et al., 2021).

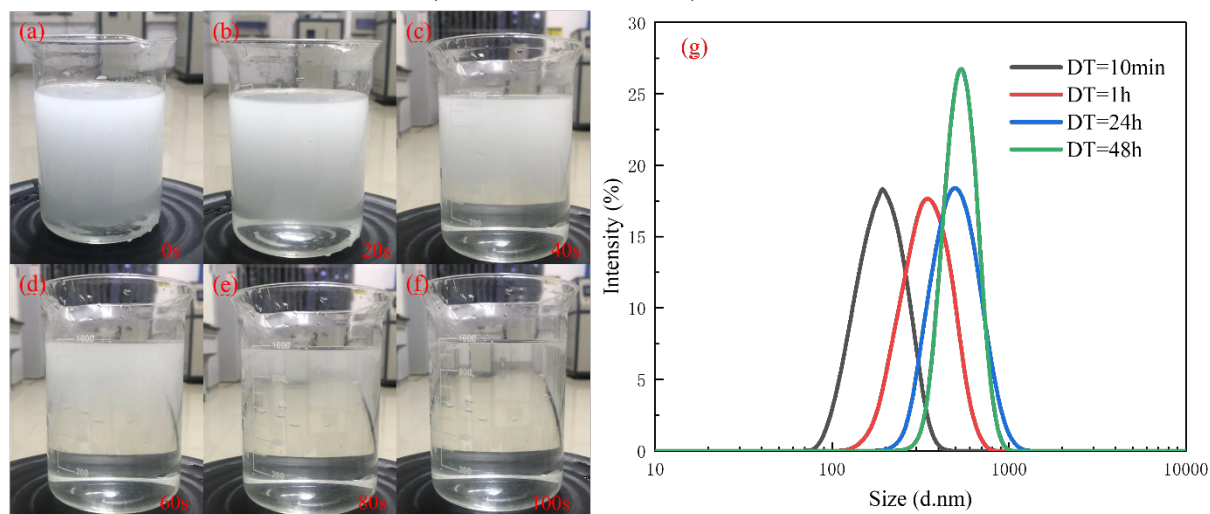


Fig. 4. Imaging and size characterization of NBs water after different deposition times (a-f: Change process of NBs water; g: Size distribution of MNBs bubbles as a function of deposition time)

#### 3.2. Effect of grinding fineness and acids type in flotation

In reverse anionic flotation, the acid slurry is the key of apatite and dolomite can well separate from each other. Fig. 5 shows the effects of different acids on concentrate  $P_2O_5$  grade and recovery. With the increase of grinding fineness, the grade and recovery of  $P_2O_5$  first increases then decreased. It is apparent from Fig. 5 that the NBs flotation achieved better performances than Tap-water flotation at higher grinding fineness, and the  $P_2O_5$  grade in the NBs increased about 1%. The  $P_2O_5$  recovery appeared to be unaffected by the NBs. But MgO content and removal also are important indexes in reverse anionic flotation. It can be seen from Fig. 6 that the NBs flotation groups reported significantly more MgO removal amount than the Tap-water flotation groups, especially. With the increase of grinding fineness, NBs flotation reduces the MgO content in concentrate by about 0.5%, and the MgO removal increases by about 6-10%.

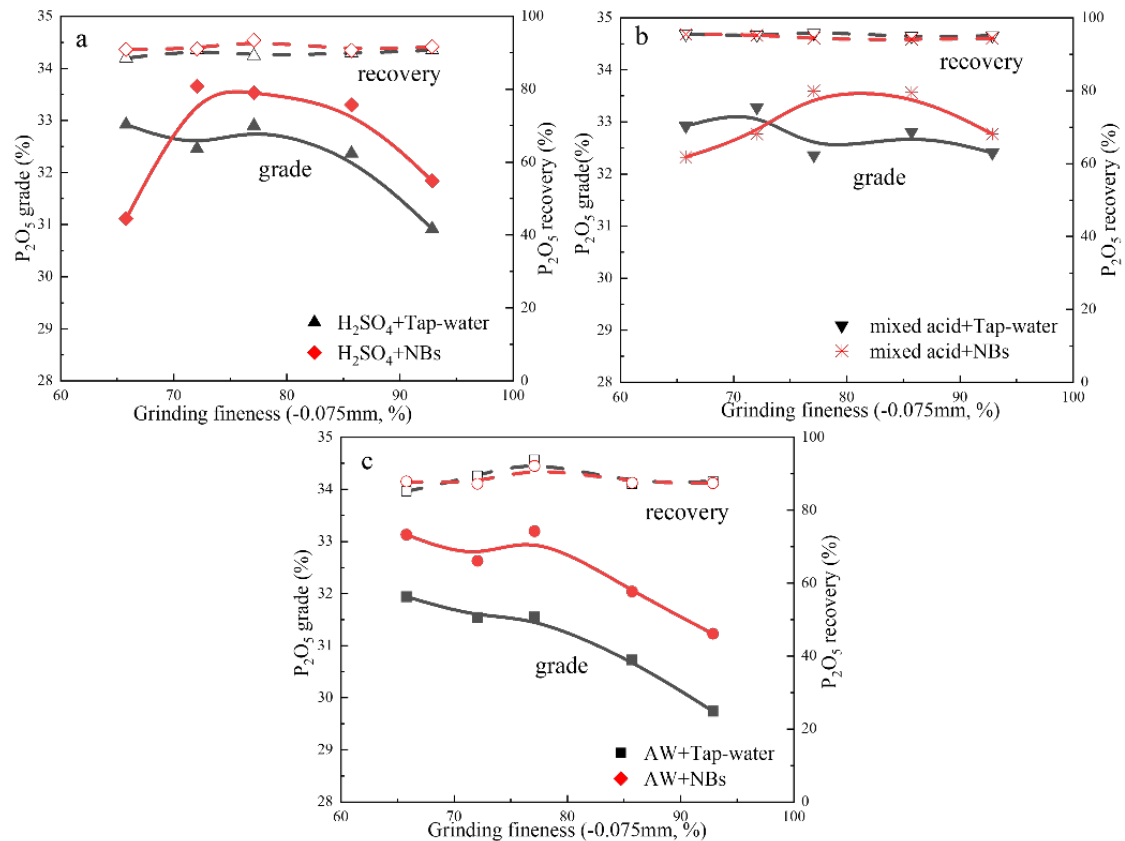


Fig. 5. Effect of acids' type on P<sub>2</sub>O<sub>5</sub> grade and recovery of concentrate (a: H<sub>2</sub>SO<sub>4</sub> dosage 10 kg/Mg; b: mixed acid dosage 10 kg/Mg; c: AW dosage 0.08 m<sup>3</sup>/Mg. GJBW dosage 400g/Mg in a, b and c)

Although the result shows the NBs flotation has better performance of reverse anionic flotation, it is significant to note that when the grinding fineness was less than -0.075mm 70%, using sulfuric acid or mixed acid to adjust pH, the indexes of NBs flotation were worse than Tap-water flotation. This particular phenomenon may be related to incomplete liberation of minerals at lower grinding fineness, and the coarse particle without adequate liberation limited the separation efficiency as well. On the other hand, the flotation performance appeared to be affected by the types of acid, the difference between NBs flotation and Tap-water flotation has a clear trend of decreasing after changing the acid's type. Even when using AW, the NBs flotation achieved better results than Tap-water flotation. Calgaroto et al. (Calgaroto et al., 2015) found that NBs enhanced the recovery rate of fine quartz particles by 20-30% and the recovery rate of coarse quartz decreased slightly. Nazari et al. (Nazari and Hassanzadeh, 2020) used dodecylamine (DDA) as a collector, pine oil (PO), methyl isobutyl carbinol (MIBC) and polypropylene glycol (A65) as frother, to research the effect of NBs on the flotation of coarse quartz. Nazari argues that DDA-NBs has a positive effect on flotation recovery, A65-NBs has an opposite effect on the flotation of coarse particles. The above researches show reagent type on the NBs flotation will affect the flotation result of coarse particles. Abouzeid et al. (Abouzeid et al., 2009) compared different acids' priority of depressing phosphate minerals, and found H<sub>3</sub>PO<sub>4</sub> has the best depression of phosphate minerals. Comparison of Fig. 5(a) and (b), in the same grinding fineness of -0.075 mm 65.78%, with the introduction of more H<sub>3</sub>PO<sub>4</sub> by mixed acid, the difference between NBs flotation and Tap-water flotation becomes smaller.

As the grinding fineness exceeds -0.075mm, both the flotation index of three acids decreased with or without NBs. Especially using AW as acid, the MgO content increased from 2.44% to 3.26% and MgO removal decreased from 73.76% to 63.26% in the absence of NBs; whereas in the presence of NBs, the MgO content increased from 1.73% to 2.36% and MgO removal decreased from 82.56% to 75.14%. This indicates that the fine particles reduced selectivity of flotation. Despite the fine particles sufficiently liberated in high grinding fineness, the negative rheological effects of pulp lead to a decrease of flotation

kinetics and an increase of fine particles' entrainment (Leistner et al., 2016; Hoang et al., 2018). In addition, the presence of NBs reduced the MgO content and improved the MgO removal in concentrate.

In general, NBs have strengthening effects in phosphate reverse flotation at higher grinding fineness, but the effect of enhanced separation at grinding fineness low is uncertain, which is worthy of further study. In this work, the NBs flotation achieved a better performance in all grinding fineness while using AW as acid to adjust the pH of pulp. The results show that the best conditions are as follows: the type of acids is AW, the grinding fineness is -0.075 mm 77.09%. Then following experiments based on this condition.

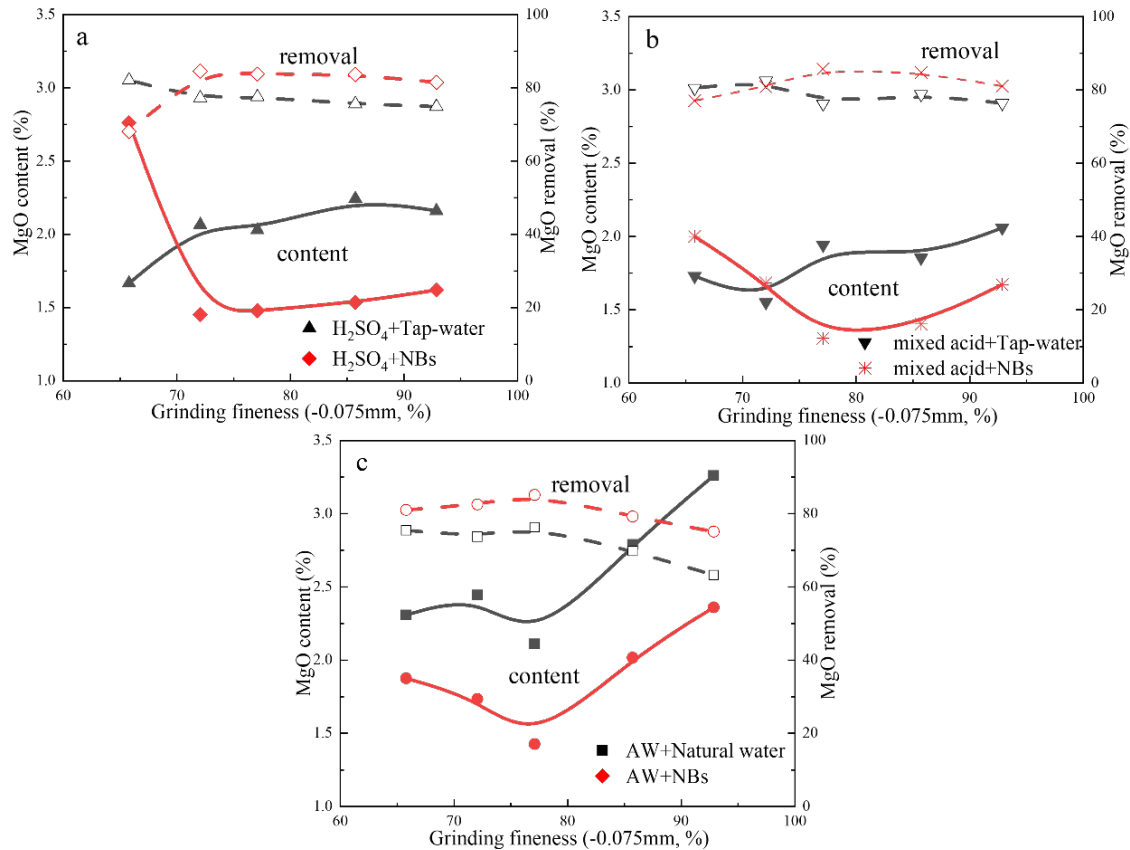


Fig. 6. Effect of acids' type on MgO content and removal of concentrate (a: H<sub>2</sub>SO<sub>4</sub> dosage 10 kg/Mg; b: mixed acid dosage 10 kg/Mg; c: AW dosage 0.08 m<sup>3</sup>/Mg, GJBW dosage 400g/Mg in a, b and c)

### 3.3. Effect of acid consumption

For the removal of dolomite, a high separation efficiency could be achieved by using reverse anionic flotation at acidic pH. Fig.7 shows the effect of AW dosage on concentrate performance parameters. P<sub>2</sub>O<sub>5</sub> grade and MgO removal rose to a high point then decreased with the increasing of AW dosage. Increasing the AW dosage from 0.04 m<sup>3</sup>/Mg to 0.08 m<sup>3</sup>/Mg, the P<sub>2</sub>O<sub>5</sub> grade increased from 28.43% to 33.19% and from 28.34% to 31.55% in the flotation with and without NBs, respectively; the MgO content dropped from 4.06% to 1.43% in the flotation with NBs and from 4.53% to 2.11% in the flotation without NBs. Further increasing the AW dosage to 0.2 m<sup>3</sup>/Mg decreased the P<sub>2</sub>O<sub>5</sub> grade to 31.95% in the NBs flotation and decreased the P<sub>2</sub>O<sub>5</sub> grade to 32.72% in the conventional flotation; the MgO content also increased gradually. The best AW dosage was 0.08 m<sup>3</sup>/Mg, the pulp pH was 5.48 at this point, NBs improved the flotation performances substantially. Abouzeid et al. (Abouzeid et al., 2009) show that the suitable pH range of pulp for reverse flotation of calcium magnesium phosphate ore is 5-6. With the enhancing of acidity of pulp, the flotation performances gradually deteriorated, and NBs flotation showed worse results than conventional flotation. This phenomenon shows that NBs cannot always enhance flotation. Lei et al. (Lei et al., 2020) reported that NBs' presence increased the entrainment rate during the flotation of kaolinite.

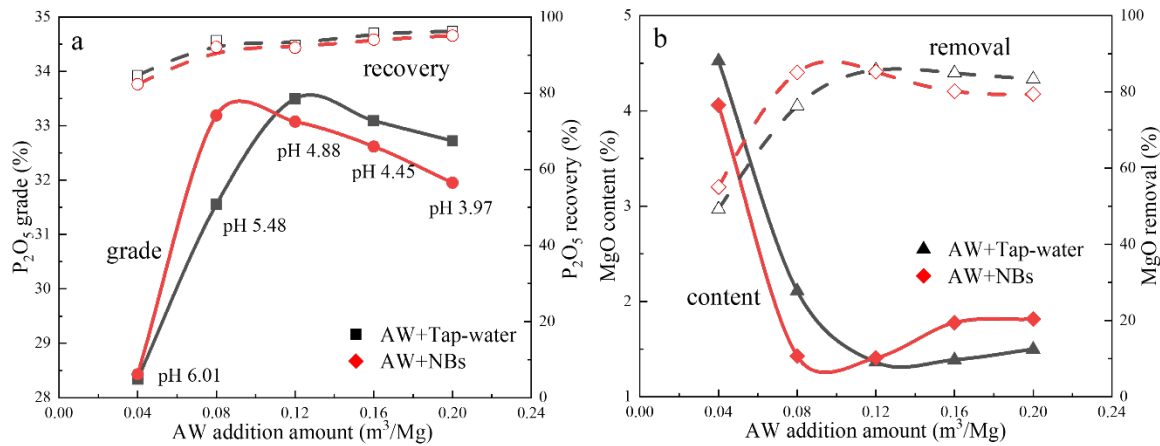
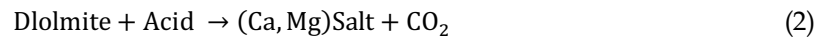
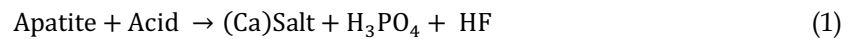


Fig. 7. Effect of acid dosage on index of reverse flotation concentrate

Various studies have assessed the efficacy of the acidic mechanism of reverse anionic flotation. Boulos et al. found that the floatability difference between apatite and dolomite became larger while the pulp pH was  $< 5.5$ , (Boulos et al., 2014). Apatite and dolomite minerals are soluble and release lattice constituents into pulp. They dissolve in acidic pulp as shown in the following chemical reaction (El-Midany et al., 2009; LIU, 2013):



$\text{H}_2\text{SO}_4$  is widely used in phosphate reverse flotation. Zou et al. (Zou et al., 2019) found that  $\text{SO}_4^{2-}$  anion can combine with Ca atoms on the apatite's surface to form  $\text{CaSO}_4$  precipitation, which hinders the adsorption of oleate on calcium sites on the surface of apatite, hence, apatite is hydrophilic. For dolomite, its surface has Mg and Ca sites that can adsorb with oleate, so that dolomite is still hydrophobic. The same author proved this theory in another study using density functional theory calculations (Cao et al., 2020). In addition, the apatite dissolves to form phosphate anions ( $\text{H}_2\text{PO}_4^-$ ) which also is considered to be the main depressants of apatite. Phosphate anions as the specifically adsorbed anion of the electrical double layer in apatite surface. It hinders the adsorption between oleate and the surface of apatite, the floatability of apatite was reduced.

Adding  $\text{H}_2\text{SO}_4$  could effectively improve the flotation indexes, but  $\text{CaSO}_4$ , the reaction product of ore with  $\text{H}_2\text{SO}_4$ , would block the pipelines (LIU, 2013). It has detrimental effects on flotation and affects the continuity of production. If there is a large amount of  $\text{CaSO}_4$  in the equipment, it is necessary to stop production and clean the equipment. The production of wet-process phosphoric acid will produce a larger number of acidic wastewater. The Wenfu Co., Ltd has used acidic wastewater in phosphate reverse flotation, and the flotation indexes were better than flotation with  $\text{H}_2\text{SO}_4$ . Calcium-precipitation was basically eliminated, the cleaning cycle of flotation equipment increased from 5 d to 15 d. The results shown in Fig.5~Fig.7 indicate that AW is available to use in flotation and NBs had pronounced effects on MgO removal but its impact on  $P_2O_5$  recovery efficiency was minimal.

### 3.4. Effect of collector consumption

GJBW, a fatty acid collector, was used as anionic collector for activated dolomite in this work and the effect of its dosage on concentrate indexes was shown in Fig. 8. In the grinding fineness of  $-0.075\text{mm}$  77.09% and AW dosage of  $0.08\text{ m}^3/\text{Mg}$ , as the collector dosage increased from  $200\text{ g}/\text{Mg}$  to  $600\text{ g}/\text{Mg}$ , the  $P_2O_5$  grade in the concentrate flotation increased from 27.48% to 33.89% without NBs, and the  $P_2O_5$  grade in the concentrate increased from 27.86% to 35.62% with NBs. It can be seen from Fig. 8(b) that NBs have a significant effect on the MgO content and removal in concentrate. NBs can reduce the MgO content by about 0.5%, and increase the MgO removal in concentrate by about 10%. Increasing the collector dosage to  $600\text{ g}/\text{Mg}$ , the content of MgO and removal were 0.97% and 93.03% with NBs; the MgO content and MgO removal were 1.36% and 86.90% with NBs. The NBs flotation results achieved the qualified index as  $P_2O_5$  grade  $> 30\%$  and MgO content  $< 1\%$  (Sis and Chander, 2003).



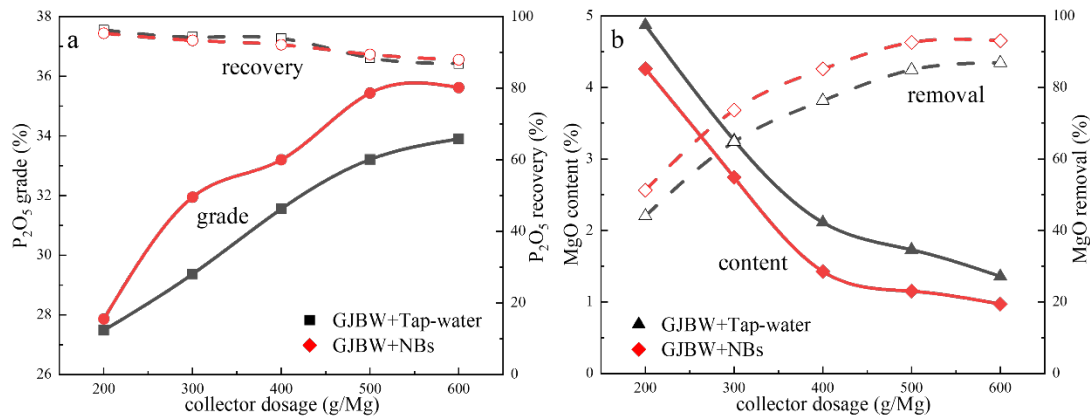


Fig. 8. Effect of collector dosage on index of reverse flotation concentrate

This may be attributed to 1) In the grinding fineness of  $-0.075$  mm 77.09%, apatite and dolomite achieved effective liberation of minerals and less associated particles. 2) Compared with conventional bubbles, NBs have smaller size (Zhang et al., 2020) and higher density (Etchepare et al., 2017), which improves the collision probability between bubbles and particles (Miettinen et al., 2010; Ding et al., 2020). 3) The adsorption of NBs on the surface of dolomite promotes the agglomeration of dolomite and increases the probability of collision between dolomite and bubbles, related studies also showed that NBs can promote the aggregation of hydrophobic calcite (Wang et al., 2019) and scheelite (Zhou et al., 2016) particles.

Closer inspection of Fig. 7 and Fig. 8 shows reducing the reagents' dosage in the presence of NBs could achieve similar flotation indexes compared without NBs. Other researchers have similar findings, Rosa et al. (Rosa and Rubio, 2018) separated of quartz and apatite mixed ores by nanobubble flotation with half dosage of collectors and depressants, the recovery of apatite is only 0.7% lower than that of ordinary water flotation under the normal reagent system. Ahmadi Rahman et al. (Ahmadi et al., 2014) found that in the presence of NBs, the flotation recovery of fine and ultra-fine chalcopyrite increased by about 16-21%, and the consumption of collectors and foaming agents decreased by 75% and 50%, respectively. The studies presented thus far provide evidence that NBs would act as "second collector" (Ahmadi et al., 2014).

### 3.5. Mechanism of NBs enhanced phosphate reverse flotation

Fig. 5-8 clearly show that the presence of NBs can improve the removal of magnesium from mid-low grade phosphate ore by reverse flotation. In the reasonable reagent system, the presence of NBs increases the removal rate of MgO by about 10% and has no significant effect on the  $P_2O_5$  grade and recovery.

Different from the adhesion of macroscopic bubbles on the mineral surface, NBs on the mineral surface have incredible stability. AFM scanning of the mineral surface shows that the morphology of NBs on the hydrophobic surface was close to flat (Seddon et al., 2010; Wang, 2018), the height was small and the solid-gas contact line was long. Lohse et al. (Lohse and Zhang, 2015) used three-phase contact line pinning theory to explain the stability of NBs on the surface. It was found that NBs with different initial contact angles would be in the same state in 3  $\mu$ s, and the equilibrium contact angle was only 2.02 (gas side). Relevant research evidence that the surface NBs can increase the contact angle of macroscopic bubbles (Calgaroto et al., 2015). Fig. 9(a)-(d) show contact angles at the water/minerals interface with and without NBs. The results showed that the nanobubble enhanced the contact angle on both apatite and dolomite surfaces. The use of NBs increased the contact angle of apatite by 27.9° and increased the contact angle of dolomite by 9.4°.

Adjusting the solution pH to 5.48 (the best result in section 3.3) by AW, the dolomite surface became hydrophobic and the apatite surface became hydrophilic, the contact angle on the dolomite surface was increased by NBs (e.g., Fig. 9(e) and (f)). In contrast, NBs cannot enhance contact angle of the apatite surface. No matter with or without NBs, macroscopic bubbles cannot adhere to the apatite surface. Zhou et al. (Zhou et al., 2020) NBs precipitation is selective and it preferential happens on hydrophobic

surfaces. Other authors proved that NBs increase the difference between hydrophilic and hydrophobic particles so that have beneficial for flotation (Tao and Wu, 2020).

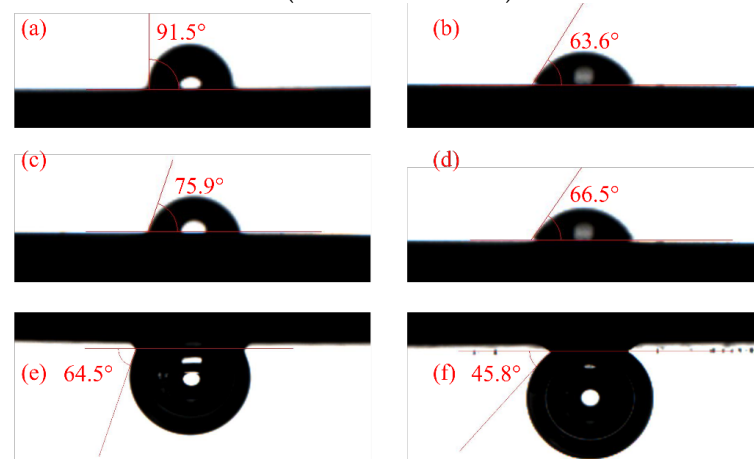


Fig. 9. (a) Contact angle of apatite with NBs. (b) Contact angle of apatite without NBs. (c) Contact angle of dolomite with NBs. (d) Contact angle of dolomite without NBs. (e) Contact angle of dolomite without NBs at pH 5.48. (f) Contact angle of dolomite without NBs at pH 5.48

Table 2. Comparing product size of flotation under different conditions (with/without NBs)

Sample / size	Foam product in conventional flotation	Foam product in NBs flotation	Dolomite	Dolomite stirred in conventional water	Dolomite stirred in NBs water
d10 ( $\mu\text{m}$ )	2.82	1.98	2.79	5.08	12.44
d50 ( $\mu\text{m}$ )	29.14	23.17	19.97	20.49	31.43
d90 ( $\mu\text{m}$ )	92.62	76.73	40.61	41.16	55.10

The result of contact angle measurement shows dolomite is hydrophobic and is the main foam product in the reverse anionic flotation. Foam products divided from the optimum flotation conditions were measured through a laser particle analyzer. Table 2 shows that the foam product size of NBs flotation was smaller than conventional flotation. In an analysis of foam product's size distribution, Pourkarimi et al. (Pourkarimi et al., 2018) found products of NBs flotation had smaller dimensions toward the conventional flotation. It can be considered that NBs have a strengthening effect on the flotation of fine particles. In a follow-up study, Hampton et al. (Hampton and Nguyen, 2010) found the NBs at the hydrophobic solid-liquid interface can connect to form a gaseous capillary bridge and a capillary force, forming a hydrophobic attraction and promoting the aggregation of fine particles; Tao et al. (Tao and Wu, 2020) thought NBs coated particles form aggregates by capillary bridge mechanism, the water film between aggregate and bubbles was faster thinning, it enhanced the probability of collision and attachment between particle and bubbles. The effect of NBs on dolomite particles was shown in Fig. 10. It was evidenced that  $d_{50}$  of dolomite increased by  $10 \mu\text{m}$ . In addition, more and larger dolomite aggregates in the pulp which was stirred in NBs water.

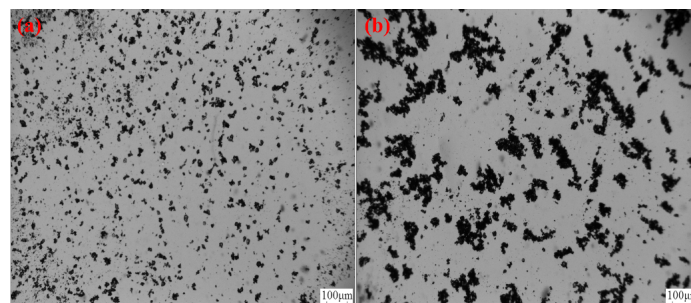


Fig. 10. Effect of NBs on particle agglomeration (a. dolomite agglomeration without NBs; b. dolomite agglomeration with NBs)

#### 4. Conclusions

Based on the above results, the effects of the NBs on reverse anionic flotation of mid-low grade phosphate ore can be drawn:

(1) NBs showed significant effects on the reverse flotation of dolomite. With the decrease of mineral particle size, the NBs flotation achieved better indexes than conventional flotation. NBs do not play a role in enhancing the separation efficiency at low grinding fineness. It may be due to a variety of reasons such as the liberation of minerals, and the types of acid, which is worthy of further study.

(2) In the optimum flotation conditions, the dolomite surface is hydrophobic and the apatite surface is hydrophilic, NBs enhanced the contact angle on the hydrophobic surface and NBs can promote the agglomeration of dolomite particles, which may be the reason NBs strengthen the reverse anionic flotation of mid-low grade phosphate ore to remove magnesium.

(3) When using acidic wastewater (AW) as regulator, the separation efficiency of flotation was stable. In the conditions of grinding fineness -0.075 mm 77.09%, AW dosage was 0.08 m<sup>3</sup>/Mg, collector GJBW dosage was 600 g/Mg, the P<sub>2</sub>O<sub>5</sub> grade and MgO content of concentrate in NBs flotation was 35.62% and 0.96%, and the P<sub>2</sub>O<sub>5</sub> grade and MgO content of concentrate in Tap-water flotation were 33.90% and 1.37%, respectively. The quality of NBs flotation products is up to the requirements for phosphate concentrate used in the wet phosphoric process.

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