The depression effect and mechanism of NSFC on dolomite in the flotation of phosphate ore

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ABSTRACT

The flotation response of collophane and dolomite using β-naphthyl sulfonate formaldehyde condensate (NSFC) as depressant has been investigated through micro-flotation and batch flotation in this paper. Their adsorption mechanisms were studied by means of zeta potential, contact angle, adsorption measurements and thermodynamics calculation. The flotation results indicated that NSFC exhibited a straining influence on the depression of dolomite and had little effect on the flotation of collophane minerals. Compared with the results achieved without the NSFC, the NSFA increased the collophane/dolomite selectivity index significantly. The zeta potential results showed a change in the zeta potential measurements of the minerals after NSFC interaction. This change was more significant in the zeta potential curves of dolomite than that of collophane. This difference is also verified by the results of the contact angle and adsorption measurements. The results of thermodynamics calculation indicated that the adsorption of NSFC at collophane and dolomite was chemisorption and physisorption, respectively. This study provides new insights into the separation of collophane minerals.

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1. Introduction

Phosphate ore production and utilization play an important role in the economic development of China. In this context, the Chine phosphate ore industry is currently focused on recovery of phosphate from low-grade ores, such as siliceous–calcareous collophane [1]. These ores are low grade in nature, containing 15–18% P_2O_5, 4–7% MgO and 25–35% SiO_2. Characterization studies have shown that the minerals are liberated at extremely fine size. The separation of collophane, a valuable mineral of phosphate ores, from impurity minerals, such as quartz and dolomite, is the most critical step in phosphate processing [2].

More than half of the worldwide production of commercial phosphate is upgraded by flotation [3]. The flotation technique for upgrading phosphate ore depends on the types of gangue minerals. When carbonate is the main gangue mineral, anionic reverse flotation showed promising results for different types of phosphate ores all over world [4–6]. In the flotation process, dolomite and calcite are floated after depressing the phosphate by suitable reagents, such as phosphoric acid, sulfuric acid and fluosilicic acid [7–9]. When silica is the main gangue mineral, the silica, which exists as quartz or sand, is often floated by cationic collectors, whereas the apatite is depressed at approximate neutral pH [10–13]. However, using cationic collectors can cause problems, such as sensitivity to slimes, and the froth collapse time is long. Thus, upgrading of ultrafine siliceous–calcareous phosphate ore via double reverse flotation is difficult.

Direct flotation of ultrafine siliceous–calcareous phosphate ore is now drawing more attention in the phosphate ore industry as an efficient improvement process. In the process, collophane is floated after depressing the silica and carbonate using fatty acids and their salts as collectors in an alkaline medium. However, the siliceous–calcareous phosphate ore is not easy to purify by flotation because the physicochemical characteristics of carbonate and the collophane surface are similar [14,15]. Meanwhile, the presence of carbonate minerals affects the flotation of silica [16,17]. Currently, the research approaches to solve this problem can be classified into two basic types: one type is to exploit high selectivity collectors, and the other type is to exploit the efficient carbonate depressants that were utilized for enhancing the separation selectivity of minerals by modifying the minerals surface characteristics.

Depressants play an important role in performing selective separation of collophane from phosphate ore by flotation. Depressants for carbonate, such as Guar gum, EDTA, modified starch, sodium lignin sulfonate and sodium humate, have been widely investigated [18–20]. However, these depressants suffered the

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disadvantage of low selectivity or high cost. Therefore, there is demand to develop more selective, inexpensive and high performance depressants for the separation of collophane from siliceous- calcareous phosphate ore.

The aim of the present study is to investigate the effect of NSFC on dolomite depression during phosphate ore flotation. The depression performance of the NSFC was evaluated by flotation experiments of pure mineral, artificially mixed sample and real phosphate ore. In addition, the adsorption mechanism of NSFC on dolomite and collophane surface was investigated by zeta potential, adsorption and contact angle measurements.

2. Experimental

2.1. Sample and reagents

2.1.1. Samples
The pure mineral sample of collophane and dolomite in this study were obtained from the Dayukou phosphate mine and the Wulongquan Mine in Hubei Province, China, respectively. The samples were crushed, handpicked with the help of microscope and then ground in a ceramic ball mill to obtain a 92 wt.% passing size of 74 μm for the flotation tests. Chemical analysis and X-ray powder diffraction data indicated that the purity of collophane was 92.05% and the purity of dolomite was 90.62%. The specific surface areas of collophane and dolomite determined by the BET test are presented in Table 1.

The phosphate ore for batch flotation tests was also obtained from the Dayukou phosphate mine. The chemical analysis results are shown in Table 2; the ore contained 18.48% P_2O_5, 4.74% MgO and 26.80% SiO_2. The mineralogical data confirmed that, in this phosphate ore, phosphate mainly exists in the form of collophane. Meanwhile, the predominate gangue minerals were dolomite and quartz.

2.1.2. Reagents
The depressant β-naphthyl sulfonate formaldehyde condensate (NSFC, >91% purity) was supplied by SOBUTE New Materials Co., Ltd. The structure of NSFC is shown in Fig. 1.

In the micro-flotation tests, NSFC was used as the depressant; sodium oleate (NaOL) was used as the collector, and hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to regulate the pH of the system. NaOL, HCl and NaOH were of analytical grade and were purchased from Kemiou Chemical Reagent Factory, China. Distilled water was used for micro-flotation, zeta-potential, adsorption and contact angle experiments.

In the batch flotation tests, NSFC was used as the depressant, sodium carbonate was used as the pH regulator and sodium oleate was used as the collector. All reagents used in batch flotation were of industrial grade. Tap water was used in the experiments.

2.2. Experiments

2.2.1. Zeta potential measurements
The zeta potentials of the minerals were measured using a Malvern Zetasizer Nano ZS90 instrument (manufactured in England). A suspension containing 0.01 wt.% mineral particles ground to −2 μm in an agate mortar was prepared in the KCl solution (10^{-3} M). The measurements were conducted at room

Table 1
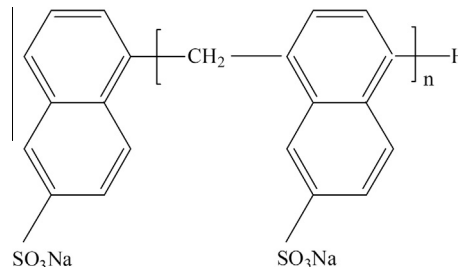Specific surface of collophane and dolomite.

Particle size (μm)	Weight (%)	Collophane (m²/g)	Dolomite (m²/g)
−74	92	1.632	2.853

Table 2
Chemical analysis results of phosphate ore (mass fraction, %).

Element	P_2O_5	MgO	Fe_2O_3	Al_2O_3	CaO	SiO_2	F	LOI
Content (%)	18.48	4.74	0.72	1.16	34.44	26.80	1.65	12.98

LOI – Loss on ignition.

Fig. 1. The structure of NSFC.

temperature (298 K). The pH value of the suspension was adjusted to a desired value using HCl or NaOH solution. In addition, measurements were also performed with the addition of depressant at a constant concentration (30 mg/dm³). The average zeta potential values of at least three independent measurements were recorded with a measurement error of ±2 mV.

2.2.2. Adsorption experiments
In this research, the amount of depressant adsorbed onto the mineral surfaces was measured by the solution depletion method using a UV–VIS spectrophotometer (UV775B, China). An amount of 1.0 g of pure mineral sample was placed in the 250 cm³ conical flask. After adding 50 cm³ of NSFC solution at a constant concentration into the suspension, the suspension was conditioned with the depressant in the Water-bathing Constant Temperature Vibrator for 1 h. Next, the solid particles were separated by a centrifuge for 12 min. The concentration of the depressant in the supernatant was measured using a UV–VIS spectrophotometer. The depressant adsorption on the mineral surface was calculated using Eq. (1).

$$\Gamma = \frac{(C_0 - C)V}{mA} \tag{1}$$

where Γ is the amount (g/m²) of the depressant adsorbed at the mineral/aqueous solution interface, C_0 and C are the initial and supernatant concentrations (g/dm³), respectively, m is the mass (g) of the mineral sample for each test, V is the volume (dm³) of the depressant solution, and A is the specific surface area (m²/g) of the particle.

2.2.3. Contact angle measurements
The contact angle of the bubbles on the surface of mineral was measured in testing solutions using the method described by Cao [21]. The mineral crystal was carefully cut (1 cm × 1 cm), and then the surface sample was polished with diamond paste. After polishing, the samples were cleaned with jets of de-ionized water and an ultrasonic water bath. The contact angle measurements of mineral were performed before and after interaction with the reagent solution at different concentration. The mineral sample was suspended in reagent solution at pH 9 for 15 min. The concentration of NSFC was 30 mg/dm³. After this time, the samples were washed with de-ionized water and then vacuum dried in desiccators for approximately 20 min. Finally, the contact angle measurements were performed. The pH value of the solution was adjusted using HCl and NaOH solutions. The measurements were performed at three