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# Influence behavior of kaolinite and illite on flotation separation of pyrite from high-sulfur bauxite

# Linyu Xu, Xianhai Li

Mining College, Guizhou University, Guiyang 550025, China

National and Local Joint Laboratory of Engineering for Effective Utilization of Regional Mineral Resources from Karst Areas, Guiyang 550025, China

Guizhou Key Lab of Comprehensive Utilization of Non-metallic Mineral Resources, Guizhou University, Guiyang 550025, China

Corresponding author: xhli1@gzu.edu.cn (Xianhai Li)

**Abstract:** Flotation separation of pyrite from high-sulfur bauxite remains challenging because of its high clay mineral content. To investigate the influence mechanisms of major clay minerals on pyrite flotation in high-sulfur bauxite, flotation tests were conducted under various conditions. Mineral liberation analysis revealed that kaolinite and illite collectively constitute ~95% of the clay minerals in a Henan high-sulfur bauxite ore. Flotation tests demonstrated their differential effects under acidic/alkaline conditions: In acidic pulp with 1×10<sup>-3</sup> mol/L sodium butyl xanthate (SBX), the actual recovery ( $\epsilon_a$ ) of kaolinite/illite-pyrite pulp was 10% lower than the theoretical recovery ( $\epsilon_T$ ). Conversely, under alkaline conditions,  $\epsilon_a$  exceeded  $\epsilon_T$  by 15-20%. Analysis showed that under acidic conditions, opposite surface charges between kaolinite/illite and pyrite caused electrostatic adsorption, occupying SBX adsorption sites on pyrite. This reduced pyrite's surface hydrophobicity and hindered hydrophobic agglomeration. Additionally, fine kaolinite/illite particles coated pyrite surfaces, blocking SBX adsorption and weakening collection efficiency. Under alkaline conditions, dissolved substances from kaolinite/illite inhibited hydrophilic substance formation on pyrite surfaces, freeing more SBX adsorption sites. Furthermore, some kaolinite/illite particles adsorbed onto pyrite surfaces and floated as "carriers" with pyrite, resulting in higher  $\epsilon_a$  than  $\epsilon_T$  in alkaline environments.

Keywords: high-sulfur bauxite, pyrite, kaolinite, illite, flotation

## 1. Introduction

Aluminum, which is mainly derived from bauxite, is an essential metal for industrial production and can be found in many applications throughout daily life (Cheng et al., 2022). The rapid industrial development in some countries, such as China, has led to an annual increase in aluminum production; however, the quantity of high-quality bauxite resources is continually decreasing. High-sulfur bauxite, which contains a sulfur content greater than 0.7 % has become an increasingly important bauxite resource (Liu et al., 2018; Xie et al., 2023). However, excessive sulfur impurities in bauxite often accelerate the corrosion of steel equipment during the alumina production process and reduce the quality and yield of alumina (Liu et al., 2021). Therefore, desulfurization is key to the clean production and low-cost utilization of high-sulfur bauxite. Current desulfurization processes include flotation desulfurization (Chimonyo et al., 2017; Zhang et al., 2023), wet desulfurization (Gu et al., 2022; Yang et al., 2023; Xu et al., 2024), roasting pretreatment desulfurization (Lou et al., 2016; Wu et al., 2020) and bioleaching desulfurization (Liu et al., 2021). Flotation is a physicochemical separation process determined by the varying surface properties of gangue and valuable minerals, whereas pyrite (FeS<sub>2</sub>) is a mineral that readily becomes hydrophobic in the presence of flotation reagents and is also the primary sulfur-containing mineral in high-sulfur bauxite (Cheng et al., 2022; Cheng et al., 2023). The flotation desulfurization is widely used because of its low cost and simple operation (Lin et al., 2020).

Generally, the bauxite with sulfur content higher than 0.7% is defined as high-sulfur bauxite (Liu et al., 2018). The reverse flotation method is generally used to desulfurize high-sulfur bauxite according to the principle of "suppressing more and floating less" (Sun et al., 2021; Cheng et al., 2023). During reverse flotation, the liberated pyrite adheres to bubbles and ascends to the foam product, known as the sulfur concentrate. Unfortunately, most high-sulfur bauxite ores are rich in clay minerals (Birinci and Gok, 2021; Long et al., 2022), which are layered silicate minerals and layered chain silicate minerals (Cruz and Peng, 2016). Owing to their brittle nature, clay minerals are prone to break and produce ultrafine particles, known as slime (-10  $\mu$ m), during the crushing and grinding process (Ramirezb et al., 2018). These slimes do not readily precipitate and form a stable suspension with a network structure within the pulp (Zhang et al., 2020). Numerous studies have shown that clay minerals can interfere with the flotation separation of sulfur-containing minerals, such as pyrite, thereby reducing the grade and recovery of sulfur from sulfur concentrate (Zhang et al., 2015; Gu et al., 2022).

Studies have focused researching the effects of clay minerals on the flotation separation of target minerals, including reagent consumption, mechanical entrainment, fine clay particle coating, and the pulp rheology caused by clay minerals. The flotation reagents are substantially consumed in the presence of fine-particle clay minerals for the reason that clay minerals with specific layered structures possess extensive surface areas that adsorb reagents during flotation, thereby reducing reagent concentration in the pulp (Chen et al., 2023); additionally, the target mineral cannot float effectively owing to insufficient adsorption. The non-selectivity of agent adsorption due to the high specific surface area of fine particles is also considered a negative factor in flotation (Pyke et al., 2003). Clay minerals often cause mechanical entrainment in the flotation pulp. A study by Wang et al. (Wang et al., 2015) indicated that the flotation grade of a copper ore decreased significantly with almost constant recovery after the addition of kaolinite. Similar conclusions were made in another study by Wang et al. (2016). The tendency for fine hydrophilic particles to adsorb into the froth layer of flotation along with interstitial films between bubbles was observed in a study by Wang and Peng (2016). Fine clay particle coatings must be considered because fine clay minerals can cover the target minerals and prevent their selective adsorption by the collector, resulting in a limited flotation effect (Arnold., 1986). For example, Peng et al. (2011) indicated that the reduction in chalcocite recovery in the presence of bentonite was caused by the covering of the surface with bentonite after the surface oxidation of chalcocite. The change in pulp rheology caused by clay minerals is also an important factor affecting the flotation of target minerals because the interaction of clay mineral particles in the flotation system dominates the pulp rheology (Zhang and Peng, 2015). Cruz et al. (2015) and Jeldres et al. (2019) showed that the flotation effect on the target minerals was worsened by the clay minerals because they caused an increase in pulp viscosity. Zhang and Xu (2015) indicated that the colloidal size and layered crystal network structure of kaolinite enhanced the degree of entrainment during flotation. These factors above pose challenges for the flotation separation of target minerals.

Some studies have focused on eliminating the influence of clay minerals on the flotation separation of the target minerals. For example, Oats et al. (2010) used hydrocyclones and dispersants to remove clay minerals and improve the recovery of target minerals, and Liu (2006) attempted to reduce clay entrainment in flotation using inorganic inhibitors or high-molecular-weight polymers, rheological measurements were used to analyze the influence of clay minerals on the rheological properties of the flotation pulp, and Ca<sup>2+</sup> ions were added to adjust the rheological properties of the pulp containing bentonite to improve pyrite flotation recovery. These methods improve flotation efficiency and the quality of the final product to some extent. However, owing to the differences between the physicochemical properties of different minerals, effective separation of all clay minerals from the target minerals cannot be achieved. Furthermore, the addition of other reagents will affect flotation in new and unknown ways. The influence of clay minerals on target minerals and the elimination of the adverse impact of clay minerals on target minerals must be further studied.

Clay minerals have a significant impact on the flotation separation of sulfur-containing minerals from high-sulfur bauxite (Farrokhpay et al., 2016; Chen and Peng, 2018; Wang et al., 2020). Unfortunately, few systematic studies have been published on the influence of clay minerals on the flotation of sulfur-containing minerals in high-sulfur bauxite under different conditions; additionally, the mechanism of influence has not been clarified. In this study, a mineralogical characterization of

high-sulfur bauxite from Henan Province, China, was performed to identify the main clay and sulfurcontaining minerals. Single-mineral flotation test methods were used to clarify the influence of the main clay minerals on the flotation separation of sulfur-containing minerals under varying flotation reagent concentrations and pulp pH values. A dynamic contact angle meter, Zetasizer Delsa Nano-C system, Optical microscope, Microcalorimeter, Time-of-flight secondary ion mass spectrometry (TOF-SIMS), and a self-built Bubble-particle attachment test system were employed to explore this influential behavior. The experimental results can provide theoretical guidance for the flotation desulfurization of the high-sulfur bauxite.

## 2. Materials and methods

## 2.1. Materials

This bauxite specimen was from a bauxite mine in Henan Province, China. The specimen was crushed to a particle size of 2 mm; then, the mineral particle size and mineral composition of this ore specimen were determined using Mineral Liberation Analysis (MLA), which was an effective method for evaluating the distribution and liberation of minerals in an ore. Subsequently, the bauxite was further ground to 0.075 mm, and its elemental composition was analyzed using an X-ray fluorescence (XRF) spectrometer (Panalytical Zetium, Malvern Panalytical, Netherlands).

Pyrite, kaolinite, and illite specimens were from a mine in Hunan Province, China. Their mineral and elemental composition was analyzed using an X-ray diffraction (XRD) analyzer (D8 Advance, Bruker, Germany) and an X-ray fluorescence (XRF) spectrometer, as detailed in Fig. 1 and Table 1, respectively. The XRD pattern of pyrite was consistent with the pyrite standard card (FeS<sub>2</sub>, JCPDS 42–1340; Fig. 1) (Hong et al., 2022). Similar matches were confirmed for kaolinite and illite. XRF analysis results for all three minerals are presented in Table 1, indicating specimen purity exceeding 90% with low impurity content, meeting the requirements of this study. To minimize the interference of particle size on the test results, pyrite, kaolinite, and illite were ground to -100  $\mu$ m using a dry ball mill. The cumulative distributions of the particle sizes of the three minerals were determined using a laser particle size analyzer (LS13320, Beckman Coulter, Inc., U.S.A.), as shown in Fig. 2. The particles of kaolinite and illite was lower than that of pyrite, resulting in a higher content of finer kaolinite and illite particles in the pulp suspension.

The resistivity of the deionized (DI) water used in the experiments of this study was 18.25 M $\Omega$  cm. The flotation reagents used in the tests, including sodium butyl xanthate (SBX) and terpineol, were purchased from Jiaxing Sicheng Chemical (Group) Company Limited (Zhejiang, China), whereas the hydrochloric acid and sodium hydroxide used for adjusting the pulp pH were purchased from Chongqing Chuandong Chemical (Group) Company.



Fig. 1. X-ray diffraction spectrum of (a) pyrite, (b) kaolinite and illite specimen

### 2.2. Methods

#### 2.2.1. Micro-flotation tests

Micro flotation tests were carried out using a flotation machine (XFGC -  $5 \sim 35$  g, Jilin prospecting machinery factory, China). 2 g single minerals (mixed minerals) specimens and 38 mL DI water were

Element/%	Fe <sub>2</sub> O <sub>3</sub>	$Al_2O_3$	SO <sub>3</sub>	K <sub>2</sub> O	MgO	SiO <sub>2</sub>	TiO <sub>2</sub>	Others
Pyrite	32.59	0.04	66.41	0.00	0.04	0.72	0.00	0.20
Illite	2.91	26.97	0.00	8.51	0.96	53.90	0.34	6.41
Kaolinite	0.17	38.49	0.00	0.32	0.04	44.64	1.72	14.62

Table 1. Chemical composition of pyrite, kaolinite and illite specimen/%



Fig. 2. Cumulative distribution of the particle size of the pyrite, kaolinite, and illite specimen

added into the cell and stirred for fully mixing. For pyrite, it was washed with an ultrasonic cleaner for 5 min to remove possible oxides on the pyrite surface (Niu et al., 2019; Hassanzadeh et al., 2021). The order of reagent addition and stirring time are shown in Fig. 3. The pH was adjusted with HCl and NaOH solution and stirred for 1 min, and a specific concentration of SBX as a collector was added and stirred for another 2 min, then 2 drops of terpineol as a frother were added to the pulp, float process was carried out for 1 min. The concentrate and tailing were filtered, dried, and weighed to calculate the flotation recovery.



Fig. 3. Flowsheet of micro-flotation test

#### 2.2.2. Zeta potential measurements

The zeta potentials of pyrite, kaolinite, and illite in the absence and presence of SBX were measured at different pH values using a Zetasizer Delsa Nano-C system (Delsa Nano C, Beckman Coulter, U.S.A) at 25 °C. During analysis, 50 mg of pyrite, illite, or kaolinite powder was mixed with 40 mL of DI water,

and the pH of the pulp was adjusted to a value of 5, 6, 7, 8, or 9. Flotation agents were added and then stirred for 5 min using a magnetic stirrer. Thereafter, the pulp was injected into a rectangular capacitor to measure its zeta potential. To ensure the accuracy of the measurement, each test was performed in triplicate and the result averaged (Demir-Yilmaz et al., 2023).

## 2.2.3. Contact angle measurements

A dynamic contact angle meter (HARKE-SPCAX3, Beijing Hake test instrument factory, China) was employed to measure the contact angle of pyrite. It was prepared by cutting to approximately  $1 \times 1 \times 1$  cm, followed by grinding and polishing sequentially with 600 cw, 800 cw, 1200 cw, and 2000 cw sandpaper. The polished pyrite blocks were immersed and stirred for 5 min in kaolinite pulp (illite pulp),  $1 \times 10^{-3}$  mol/L SBX solution at pH 5 or pH 9. Then the specimen was removed, dried at room temperature, and used to measure the intermediate contact angle.

## 2.2.4. Optical microscope observation

Flotation pulp samples were prepared following micro-flotation test conditions: 2 g single mineral (or mixed mineral) specimens were added to 38 mL deionized water to create four pulp systems at pH 5 and pH 9, both with and without SBX. Using a rubber-bulb pipette, 1-2 drops of uniformly mixed pulp were deposited onto glass slides. Particle dispersion states were subsequently examined under an optical microscope (CX31, OLYMPUS, Japan).

## 2.2.5. Bubble-particle wrap angle measurements

A self-built bubble-particle attachment test system was used to measure the bubble-particle wrap angle (BPWA); schematic illustrations of the testing principle and the bubble-particle attachment test system is shown in Fig. 4. This test system was composed of a rectangular quartz glass cuvette (dimensions of  $3.5 \times 3.5 \times 5$  cm), a needle capillary (internal of diameter 2 mm), a micro syringe pump, a camera, magnetic stirrer, and a computer (Huang and Zhang, 2023).

During the testing process, the specimens (0.5 g) and 40 mL of DI water were added to the quartz glass cuvette, stirred for 1 min to mix the mineral particles, then left to stand for 2 min. Air was injected into the pulp using an injection pump and microsampler to generate air bubbles with a diameter of approximately 4 mm. The rotor speed of the magnetic stirrer was set at 250 rpm. The pulp was allowed to stand after varying mixing durations. Thereafter, the wrapping angle of the particles on the bubble surface was measured by capturing bubble images using a camera connected to a computer.



Fig. 4. (a) Schematic diagram and (b) the picture of the bubble-particle attachment test system

### 2.2.6. Reaction heat measurements

The reaction heats of pyrite and DI water, kaolinite pulp supernatant (KPS), or the illite pulp supernatant (IPS) were tested using a membrane mixing cell in a microcalorimeter (C80, Setaram, France). The liquid and powder specimens were placed in the upper and lower pools, respectively, which were separated by a Teflon film (Fig. 5). The quantity of the solution volume and powder specimen was 2.5 mL and approximately 50 mg, respectively. The test was conducted as follows: the specimens were heated from 20–30 °C at a rate of 0.2 °C/min, then the temperature remained at 30 °C for 5000 min. Powder specimens were reacted with liquid specimens at a temperature of 30 °C. After the heat flow baseline was stabilized, a mechanical stirring rod was used to break the film to allow the liquid from the upper cell to flow into the lower cell; the liquid was mixed by rotating the stirrer for three cycles. The change in the heat flow baseline was detected using microcalorimeter software, and the test was stopped once re-stabilization occurred. The microcalorimeter software was used to calculate the reaction heat, which was the total reaction heat during the interaction of pyrite and DI water, KPS, and IPS.



Fig. 5. (a) Picture of C80 microcalorimeter; (b) a pair of membrane mixing cells made with Hastelloy in this study; (c) internal structure of the membrane mixing cell

## 2.2.7. TOF-SIMS measurements

TOF-SIMS (ION-TOF GmbH, Münster, Germany) is a high-resolution measurement technique in which a low quantity of secondary ions is expelled from the surface of a specimen after its excitation with primary ions. The mass of the ions is then determined based on the time of arrival of various secondary ions to the detector. The arrival times differed because of the varying ion masses of the secondary ions; these differences are used to examine the chemical composition of KPS or the surface of pyrite that reacted with DI water. The following test conditions were applied: the grating area of the specimen surface detected by mass spectrometry was 200  $\mu$ m × 200  $\mu$ m; the primary ion beam and the current were 30 KeV Bi<sup>+</sup> and 2 nA, respectively; C<sup>+</sup>, CH<sub>3</sub><sup>+</sup>, Fe<sup>+</sup>, and C<sup>-</sup>, CH<sup>-</sup>, S<sup>-</sup> were used as the calibration points in the positive and negative ion modes, respectively (Zhao et al., 2022).

## 3. Results and discussion

## 3.1. Ore properties

The mineral and chemical compositions of the bauxite are listed in Tables 2 and 3, respectively. The main useful minerals in this high-sulfur bauxite were the diaspores; additionally, the main gangue minerals included pyrite, clay minerals, anatase, and quartz, of which the main clay minerals were illite and kaolinite, accounting for approximately 95 %. The pyrite content was 2.81 %, whereas that of illite

and kaolinite were 11.53 % and 4.91 %, respectively. Illite and kaolinite exhibited significant influences on the properties of the pulp (Zhang and Peng, 2015). As shown in Table 3, the Al<sub>2</sub>O<sub>3</sub> content, A/S ratio, and total sulfur content were 58.92 %, 4.12, and 1.12 %, respectively. The main sulfur-containing mineral in the high-sulfur bauxite was pyrite (Table 2). These results were consistent with the characteristics of clay and sulfur-containing minerals in high-sulfur bauxite (Chai et al., 2018; Cheng et al., 2023). Therefore, this study focused on pyrite and clay minerals (kaolinite and illite), and their interactions in the flotation separation processing.

The MLA of the bauxite was shown in Fig. 6. The quantity of pyrite embedded in illite, kaolinite, and diaspore was 17.57%, 7.49%, and 53.67 %, respectively. In addition, the quantity of diaspore embe-

Table 2. Mineral composition of high-sulfur bauxite										
Minerals	Diaspore	Goethite	Quartz	Dolomite	Pyrite	Illite	Kaolinite	Chlorite	Others	
Content/%	72.59	3.80	0.54	0.83	2.81	11.53	4.91	0.16	2.83	

Table 3. Chemical composition of high-sulfur bauxite												
Element	$Al_2O_3$	$SiO_2$	TFe <sub>2</sub> O <sub>3</sub>	$SO_3$	TiO <sub>2</sub>	K <sub>2</sub> O	CaO	MgO	MnO	Na <sub>2</sub> O	NiO	$P_2O_5$
Content/%	58.92	14.31	3.84	2.79	2.66	2.01	1.17	0.57	0.02	0.06	0.01	0.15



Fig. 6. MLA automated mineral parameter analysis diagrams (a: total MLA analysis of high-sulfur bauxite; b: MLA analysis of the total map corresponding to the backscattering map; c: pyrite particle embedding relationship diagram; d: the diagram of mineral embeddedness in bauxite; e: the distribution of the particle size of the bauxite)

dded in illite and kaolinite was 58.02% and 6.47%, respectively. Due to the significantly higher hardness of pyrite and diaspore compared to kaolinite and illite, substantial amounts of fine-particle kaolinite (or illite) will be generated during mineral liberation through grinding (Lu, 2012; Mañosa et al., 2023). Unfortunately, the presence of these fine particles increases the difficulty of flotation, which is a common challenge in flotation research (Peng et al., 2023). Particularly when <10 µm particles coat valuable minerals, they exert markedly adverse effects on the reverse flotation of pyrite (Li et al., 2018). Based on these findings, this study selected single-mineral specimens of pyrite, kaolinite, and illite to systematically investigate the impact of clay minerals on pyrite flotation separation. These minerals were ground to 100 µm in diameter for the following experiments.

#### 3.2. Single-mineral flotation

Single-mineral flotation experiments were conducted to simulate the flotation behaviors of pyrite, kaolinite, and illite during the reverse flotation of high-sulfur bauxite. SBX was used in this experiment to test the floatability of the three minerals because it is a frequently used desulfurization reagent in high-sulfur bauxite reverse flotation processes (Yu et al., 2016; Wang et al., 2023). The flotation effects of pyrite, illite, and kaolinite were investigated under different SBX concentrations and natural pH conditions. The effects of pH on the flotation recoveries of pyrite, illite, and kaolinite were further explored. Pyrite exhibited favorable natural floatability, and its recovery increased with increasing SBX concentration, reaching values greater than 90 % when the concentration of SBX was increased to 1×10-<sup>3</sup> mol/L (Figure 7 (a)). Subsequently, pyrite recovery decreased. Changes in the SBX concentration exhibited a limited effect on the flotation recoveries of illite and kaolinite. This indicated that SBX could not collect illite and kaolinite; therefore, in theory, SBX was a good flotation agent for the separation of pyrite and clay minerals.

At pH 3, 66.64 % of pyrite was recovered; however, this decreased to 53.62 % as the pH value increased to 7 (Fig. 7 (b)). The flotation recovery of pyrite remained at approximately 20 % in an alkaline solution. Therefore, this condition was not favorable for the flotation separation of pyrite because the hydrophilic substances (Fe-OH) produced on the surface of pyrite by the interaction of OH<sup>-</sup> in the solution and Fe from pyrite prevented the adsorption of SBX (Bicak et al., 2007); Moreover, the OH<sup>-</sup> moiety on the surface of pyrite exhibited a strong bonding force with Fe, which could compete with the SBX ions in solution for adsorption on the Fe sites and even displace the already adsorbed SBX ions from the surface of pyrite and inhibit the formation of double xanthates (Mu et al., 2016). The flotation recoveries of illite and kaolinite did not change significantly with changing pH. These recoveries remained at approximately 20 %, demonstrating that the effect of pH on the flotation of kaolinite and illite was limited. Therefore, the recovery of pyrite was greater under acidic conditions and at a  $1 \times 10^{-3}$  mol/L SBX concentration.



Fig. 7. Effect of SBX concentration and pulp pH on the flotation recovery of pyrite, illite, and kaolinite (a: SBX concentration; b: pulp pH)

The theoretical flotation recovery of mixtures (pyrite-kaolinite mixture or pyrite-illite mixture) was defined as follows (Yin and Wang, 2014; Bilal et al., 2021):

$$\varepsilon_{\rm T} = \varepsilon_1 \gamma_1 + \varepsilon_2 \gamma_2 \tag{1}$$

where  $\varepsilon_1$  and  $\varepsilon_2$  represent the recoveries of kaolinite (or illite) and pyrite, respectively, during the flotation test. The mass fraction of kaolinite (or illite) and pyrite in the mixture are represented by  $\gamma_1$  and  $\gamma_2$ , respectively ( $\gamma_1 + \gamma_2 = 1$ ). When the actual flotation recoveries ( $\varepsilon_a$ ) of the mixtures were approximately equal to  $\varepsilon_T$ , the kaolinite (or illite) particles were assumed to not have affected the flotation of pyrite. On the other hand, kaolinite (or illite) may interact with pyrite and affect its floatability.

To investigate the effect of mass ratios of pyrite : illite and pyrite : kaolinite mixtures on pyrite flotation, mixed minerals with varying proportions were prepared to examine the impact of clay mineral content (Fig. 8). The  $\varepsilon_T$  of mixed minerals was calculated using Eq. (1). The  $\varepsilon_a$  gradually decreased with increasing kaolinite proportion (Fig. 8(a)), and when the kaolinite mass fraction exceeded >20%,  $\varepsilon_a$  remained consistently lower than  $\varepsilon_T$ . This demonstrates that kaolinite particles exert significant inhibitory effects on pyrite flotation, with this inhibition intensifying as kaolinite mass fraction increases. Similarly, illite substantially inhibits pyrite flotation separation, though this effect is more pronounced at lower mass fractions – a 20.02% recovery reduction occurs at merely 20% illite mass fraction. Therefore, at pH 5, kaolinite (or illite) constitutes a critical factor affecting pyrite flotation.



Fig. 8. Effect of kaolinite or illite mass fraction on the flotation recovery of mixtures (a: pyrite-kaolinite mixture; b: pyrite-illite mixture)

Considering the effect of kaolinite (or illite) on pyrite flotation, the effects of different SBX concentrations and pH conditions on the flotation recovery of the mixture were explored by maintaining the percentage of kaolinite (or illite) at 40 % (Figs. 9 and 10). The  $\varepsilon_a$  value of the mixture was lower than the  $\varepsilon_T$  value regardless of the amount of SBX added (Fig. 9). The addition of SBX did not alter the inhibition of pyrite by kaolinite (or illite). The  $\varepsilon_a$  value of the mixtures of kaolinite (or illite) and pyrite were significantly greater than the  $\varepsilon_T$  values under alkaline conditions (Fig. 10), which indicated that pyrite and kaolinite (or illite) interacted under alkaline conditions, and the mixture was easier to float than the single mineral. Previous studies assumed that the coarse and fine particles agglomerate, and the coarse mineral particles act as "carriers" for fine mineral particles when the  $\varepsilon_a$  value of the mixture was greater than the  $\varepsilon_T$  value (Li et al., 2017; Bilal et al., 2021). However, other factors may contribute to these results, which will be discussed in subsequent studies.

## 3.3. Zeta potential

Fig. 11 shows the zeta potential of pyrite, illite, and kaolinite as a function of pH in the absence and presence of SBX. As shown in the figure, the surface potential of pyrite was negative after the addition of SBX because this compound is an anionic trapping agent. Under acidic conditions, SBX decomposes into SBX ions ( $C_4H_9OCSS$ -), which undergo strong chemical adsorption onto the surface of positively



Fig. 9. Effect of SBX concentrations on the flotation recovery of pyrite-kaolinite mixture and pyrite-illite mixture when the mass fraction of kaolinite (or illite) was 40% (a: pyrite-kaolinite mixture; b: pyrite-illite mixture)



Fig. 10. Effect of pH on the flotation recovery of the pyrite-kaolinite mixture and pyrite-illite mixture when the mass fraction of kaolinite (or illite) was 40% (a: pyrite-kaolinite mixture; b: pyrite-illite mixture)

charged pyrite (Yin et al., 2018). This led to an exponential reduction in the zeta potential of the pyrite surface to a value lower than zero. Moreover, the adsorbed C<sub>4</sub>H<sub>9</sub>OCSS- on the pyrite surface was highly hydrophobic. The pyrite surface exhibited strong hydrophobicity after C<sub>4</sub>H<sub>9</sub>OCSS- adsorption. After colliding with the bubbles, the probabilities of adhesion and detachment increased and decreased, respectively. This explains the high recovery of pyrite flotation under acidic conditions (Fig. 7). Unfortunately, the pyrite surface is negatively charged under neutral and alkaline conditions. This was mainly because the outermost iron (Fe3) 3d state on the pyrite surface was near the Fermi energy level, indicating that the outermost iron atoms on the pyrite surface were highly reactive. An electron donor is readily adsorbed by iron atoms on the surface; thus, pyrite readily interacts with hydroxide ions (the electron donor) in an alkaline medium to form iron hydroxide on the surface (Bicak et al., 2007). Owing to electrostatic repulsion, the adsorption of SBX onto the pyrite surface to form hydrophobic substances is challenging, which is consistent with the conclusions of previous studies.

The surfaces of kaolinite (or illite) are negatively charged. The effect of pH on the surface electrical properties of kaolinite and illite is limited. Electrostatic repulsion always inhibits chemical adsorption between the collector and kaolinite (or illite). Therefore, the flotation recoveries of kaolinite (or illite) do not change significantly, regardless of the SBX concentration or the pH conditions. However, the electronegativity of kaolinite (or illite) is relatively strong. Under acidic and alkaline conditions, the electrostatic repulsion between the particles was strong, which resulted in the easy dispersion of kaolinite (or illite) in the pulp and affected the surface properties of pyrite. Under acidic conditions, the

pyrite surface was positively charged before the addition of SBX; therefore, the negatively charged kaolinite and illite were adsorbed on the pyrite surface, hindering the adsorption of SBX. Consequently, the actual recoveries of the pyrite-kaolinite and pyrite-illite mixtures were lower than the theoretical recoveries under acidic conditions.



Fig. 11. Zeta potentials of pyrite, illite, and kaolinite in the absence and presence of 1 × 10-3 mol/L SBX as a function of pH

## 3.4. Contact angle

Fig. 12 shows the contact angles of pyrite after soaking in kaolinite and illite suspensions under different pH conditions, both in the absence and presence of SBX. Generally, the bigger the contact angle, the worse the wettability and the better the floatability. However, when the contact angle was relatively small, the opposite effect was observed (Zhao et al., 2024). In Fig. 12, points A, B, C, and D represent the contact angles of pyrite, pyrite soaked in illite pulp, pyrite soaked in kaolinite pulp, and pyrite soaked in  $1 \times 10^{-3}$  mol/L SBX solution, respectively. At pH 5, the contact angle of pyrite increased to 112.3°, confirming the research results of SBX enhancing the surface hydrophobicity of pyrite in the previous study (Deng et al., 2021). After soaking in kaolinite and illite pulps, the contact angles of pyrite decreased to 40.3° and 48.6°, respectively. This significant reduction indicated that both kaolinite and illite had significantly reduced the hydrophobicity of the pyrite surface, thereby affecting the floatability of pyrite.

The contact angle of pyrite after soaking in a 1 × 10<sup>-3</sup> mol/L SBX solution at pH 9 decreased by 34.3° compared with that at pH 5. However, the contact angle of pyrite after soaking in the illite pulp did not change significantly. Conversely, the contact angle of pyrite increased significantly after soaking in kaolinite pulp. These results suggested that, compared with acidic conditions, alkaline conditions were detrimental to the adsorption of SBX onto the pyrite surface. However, the presence of kaolinite (or illite) under alkaline conditions did not significantly affect the wettability of the pyrite surface.

The microscopic morphology of the particles in the suspensions of pyrite, pyrite-illite, and pyritekaolinite at pH = 5 and pH = 9 in the presence and absence of SBX were observed using optical microscopy (Fig. 13). The addition of SBX increased the hydrophobicity of the pyrite surface at pH = 5, resulting in the "hydrophobic agglomeration" of pyrite particles (Fig. 13 (a), (b), (g), and (h)). This phenomenon has been observed in many studies (Wang et al., 2021; Xue et al., 2021; Shen and Zhang, 2022). However, the agglomeration phenomenon was not clearly observed despite the addition of SBX at pH 9. This was mainly due to the hydrophilic substances generated on the pyrite surface under alkaline conditions. A proportion of kaolinite (or illite) was dispersed in the pulp, whereas another proportion adhered to the surface of pyrite (Fig. 13 (c)–(f)). This phenomenon further supports the previous conclusion (section 3.3) that negatively charged kaolinite and illite can be readily adsorbed onto the positively charged pyrite surface. The same solution conditions (pH = 5 and  $1\times10^{-3}$  mol/L SBX) prevent the "hydrophobic agglomeration" of pyrite, which results in a lower  $\varepsilon_a$  value than the  $\varepsilon_T$  value under acidic conditions. The distribution density of fine-particle kaolinite or illite particles in close proximity to pyrite in the mixed kaolinite-pyrite and illite-pyrite pulp suspensions is relatively high (red circles in Figs. 13 (j) and (l)). This suggested that many kaolinite and illite particles formed a protective "armor" by wrapping around the pyrite particles.



Fig. 12. Effect of fine particle kaolinite and illite on the contact angle of pyrite surface at pH=5 and pH=9



Fig. 13. Microscopic morphology of pyrite, pyrite-kaolinite, and pyrite-illite pulp at pH=5 and pH=9 in the presence and absence of 1×10-3 mol/L SBX

## 3.5. Bubble-particle wrap angle

BPWA was first introduced by Chu et al. (Chu et al., 2014). which was a macroscopic reflection of particles adhering to a bubble. This method was employed to simulate the flotation process and represent the interaction between particles and bubbles. Subsequently, Huang et al. (Huang and Zhang, 2023) successfully characterized the effect of fine dolomite particles on fluorapatite flotation using BPWA. To further understand the effect of kaolinite and illite on pyrite flotation, BPWA was used to assess the influence of kaolinite and illite on the adhesion of pyrite to the bubbles. Flotation is a very

complex physicochemical process. The surface properties of the target minerals and the interference of other minerals on the surface properties of the target minerals directly affect the interaction between the target mineral particles and bubbles in the flotation process, which is the key factor affecting mineral flotation separation. In this test, the minerals (0.5 g) were accurately weighed in each test to eliminate the interference of mineral mass on the test results. To a container, 0.5 g fine particle pyrite or a 0.5 g mixture (0.4 g fine particle pyrite and 0.1 g fine particle kaolinite (or illite)) and 40 mL of DI water were added, then the mixture was thoroughly stirred. The BPWAs were collected at wrapping times ( $T_w$ ) of 10, 30, 60, 120, and 180 s.  $T_w$  was defined as the stirring time required to facilitate the attachment of particles onto the bubble. The BPWAs of pyrite, the pyrite-kaolinite mixture, and the pyrite-illite mixture under different conditions are shown in Fig. 14–Fig. 17.



Fig. 14. BPWAs of pyrite, pyrite-kaolinite mixture, and pyrite-illite mixture at different T<sub>w</sub> when pH=5 in the absence of SBX (a: pyrite; b: pyrite-kaolinite mixture; c: pyrite-illite mixture; d: BPWA kinetics of pyrite at pH=5)



Fig. 15. BPWAs of pyrite, pyrite-kaolinite mixture and pyrite-illite mixture at different T<sub>w</sub> when pH=5 in the presence of 1×10<sup>-3</sup> mol/L SBX (a: pyrite; b: pyrite-kaolinite mixture; c: pyrite-illite mixture; d: BPWA kinetics of pyrite at pH=5)

The BPWA of pyrite, pyrite-kaolinite mixture, and pyrite-illite mixture first increased and then decreased with the increase of  $T_w$  at pH=5 (Fig. 14). The BPWA of pyrite was the biggest and most stable at pH=5, which indicated that the natural hydrophobicity of pyrite was greater than those of kaolinite and illite. The hydrophobicity of pyrite particles was greatly enhanced in the presence of 1×10<sup>-3</sup> mol/L SBX, and the BPWA increased by 126° compared to that in the absence of SBX when the  $T_w$  was 60 s (Fig. 15), which indicated that SBX had a strong ability to collect pyrite particles. Furthermore, the BPWA of the pyrite-kaolinite mixture and pyrite-illite mixture also increased, but the increment was much smaller than that of pyrite. It was especially worth noting that the BPWAs of the pyrite-kaolinite

mixture and pyrite-illite mixture were lower than 20% (proportion of pyrite in the mixture) of that of pyrite with the extension of  $T_w$ , such as in the case of 120 s and 180 s in the absence of SBX or 60 s, 120 s, and 180 s in the presence of 1×10<sup>-3</sup> mol/L SBX, which further indicated that kaolinite (or illite) obstructed the adsorption of pyrite on the bubble at pH=5.

The BPWAs of pyrite, the pyrite-kaolinite mixture, and the pyrite-illite mixture were low at pH 9 in the absence of SBX (Fig. 16). The maximum BPWA of pyrite was 64° at pH 9, which was significantly lower than the minimum BPWA of pyrite (90°) at pH 5. This indicated that pyrite was hydrophilic under alkaline conditions, and the floatability was significantly reduced. The BPWAs of pyrite, the pyritekaolinite mixture, and the pyrite-illite mixture increased significantly with the addition of  $1 \times 10^{-3}$  mol/L SBX, and increased with increasing T<sub>w</sub> (Fig. 17). The increasing trend of the BPWA of pyrite in the presence of  $1 \times 10^{-3}$  mol/L SBX at pH 9 was not observed at pH 5, further illustrating that pyrite was strongly inhibited under alkaline conditions. The BPWAs of the pyrite-kaolinite and pyrite-illite mixtures were significantly higher than those of pyrite at pH 9, whereas the BPWAs were significantly lower than those of pyrite at pH 5, which further demonstrated that kaolinite and illite enhanced the adhesion of pyrite on the bubble under alkaline conditions.



Fig. 16. BPWAs of pyrite, pyrite-kaolinite mixture, and pyrite-illite mixture at different T<sub>w</sub> when pH=9 in the absence of SBX (a: pyrite; b: pyrite-kaolinite mixture; c: pyrite-illite mixture; d: BPWA kinetics of pyrite at pH=5)



Fig. 17. BPWAs of pyrite, pyrite-kaolinite mixture and pyrite-illite mixture at different T<sub>w</sub> when pH=5 in the presence of 1×10<sup>-3</sup> mol/L SBX (a: pyrite; b: pyrite-kaolinite mixture; c: pyrite-illite mixture; d: BPWA kinetics of pyrite at pH=9)

## 3.6. Reaction of pyrite with suspension

The reaction heats of pyrite and KPS, IPS, and DI water under acidic and alkaline conditions were measured to examine the effects of kaolinite and illite on the physical or chemical reactions occurring

on the surface of pyrite (Fig. 18). The reactions of pyrite with KPS, IPS, and DI water at pH 5 were exothermic (Fig. 18 (a)), mainly because the oxides on the surface of pyrite (the reaction products of pyrite and  $O_2$ ) reacted with H<sup>+</sup> in acidic solutions, releasing heat (Liu et al., 2021). The reaction heats of the reactions of pyrite with KPS, IPS, and DI water under acidic conditions were similar at approximately 10 J/g, indicating that the substances in KPS and IPS have a relatively small effect on the surface of pyrite, while H+ plays a dominant role on the surface of pyrite. The reaction heat between pyrite and DI water at pH 9 was 2.894 J/g (Fig. 18 (b)), which was mainly caused by a combination of the following reactions: the action of the water molecules on the surface of pyrite and the hydrolysis of pyrite crystals to ferrous hydroxide (Eq. 2), which released ferrous ions. These ions subsequently interacted with OH<sup>-</sup> to produce iron hydroxide (Eq. 3) (Xue et al., 2021).

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$$
 (2)

$$Fe(OH)_2 + OH^- \leftrightarrow Fe(OH)_3 + e^-$$
(3)

Furthermore, the reaction heats of the reactions of pyrite with KPS and IPS at pH 9 were 8.785 and 7.065 J/g, respectively, which were higher than those of pyrite with DI water. These data show that the substances in KPS and IPS at pH 9 were involved in the reaction on the surface of pyrite; therefore, the effect of this reaction on the surface properties of pyrite could not be neglected.



Fig. 18. Reaction heats of pyrite and KPS, IPS, and DI water (T=30°C; a: at pH=5; b: at pH=9)

Fig. 19 showed the TOF-SIMS positive and negative mass spectra for the reaction of pyrite with DI water and KPS at pH 9 in the mass range of 0–200 m/z, respectively. This experiment aimed to further confirm the reaction mechanism of the dissolved ions of kaolinite and pyrite. The NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+,</sup> and Fe<sup>+</sup> in the positive mass spectra were pronounced (Fig. 19 (a)). The representative peaks in the negative mass spectrum exhibited signals for O<sup>-</sup>, OH<sup>-</sup>, S<sup>-</sup>, SO<sub>3</sub><sup>-</sup>, FeS<sup>-</sup>, SO<sub>4</sub><sup>-</sup>, and HSO<sub>4</sub><sup>-</sup> (Fig. 19 (a)). Moreover, the peaks for Fe<sup>+</sup> and S<sup>-</sup> increased at 56 and 32 m/z, respectively, which originated from pyrite. Therefore, part of the FeS<sub>2</sub> on the surface of pyrite at pH 9 was oxidized to sulfur oxides and hydroxides, which further confirmed the presence of the hydrophilic substance, Fe(OH)<sub>2</sub>/Fe(OH)<sub>3</sub>, on the surface of pyrite in an alkaline environment.

Normalized peak intensities are generally used to compare the abundance of species on the specimen surface (Bai et al., 2019; Lai et al., 2022). Fig. 20 shows the TOF-SIMS normalized peak intensities of the main positive and negative ions on the surface of pyrite that reacted with DI water and KPS at pH 9, respectively. The peak intensity of the positive fragment ion, Fe<sup>+</sup>, on the surface of pyrite that reacted with KPS was greater than that of DI water at pH 9 (Fig. 20); additionally, the peak intensities of the negative fragment ions, O<sup>-</sup>, S<sup>-</sup> and SO<sub>3</sub><sup>-</sup>, on the surface of pyrite that reacted with KPS were marginally greater than those on the surface of pyrite that reacted with DI water at pH 9. Therefore, the surface of pyrite that reacted with KPS exhibited stronger S<sup>-</sup> and Fe<sup>+</sup> peak intensities than those of DI water at pH 9. This difference was greater for Fe<sup>+</sup>, which was the main active site for SBX adsorption on the surface of pyrite (Haung and Miller, 1978; Pecina et al., 2006). This shows that the substances in KPS were involved in the reaction on the pyrite surface and inhibited the production of Fe(OH)<sub>2</sub>/Fe(OH)<sub>3</sub>, thereby

enhancing the reaction of SBX on the pyrite surface. This might be a critical factor for the higher  $\epsilon_a$  value than the  $\epsilon_T$  value of the pyrite-kaolinite mixture under alkaline conditions.

In summary, the influence mechanism of clay minerals (illite/kaolinite) on pyrite flotation is illustrated in Fig. 21. In an acidic solution, H<sup>+</sup> reacts with the iron oxide on the pyrite surface, exposing



Fig. 19. TOF-SIMS spectra on the surface of pyrite reacted with DI water and KPS at pH=9 (a: positive ion spectra; b: negative ion spectrum)



Fig. 20. Normalized peak intensities on the surface of pyrite surface reacted with DI water and SBX at pH=9



Fig. 21. Schematic illustration of the influence behavior of clay minerals (illite/ kaolinite) on the flotation separation of pyrite

fresh surfaces that facilitate the chemical adsorption of SBX and hydrophobic agglomeration. However, kaolinite/illite carries an opposite surface charge to pyrite, and their adsorption onto pyrite hinders the collecting effect of SBX while enhancing the surface hydrophilicity of pyrite through encapsulation. In an alkaline solution, the hydrophilic substance, Fe(OH)<sub>2</sub>/Fe(OH)<sub>3</sub>, was formed on the pyrite surface, and electrostatic repulsion with SBX reduces floatability. However, dissolved components from clay minerals inhibit the formation of hydrophilic substances, providing more SBX adsorption sites and thereby promoting the floatation of pyrite.

## 4. Conclusions

The effects of kaolinite and illite on the flotation separation of pyrite in high-sulfur bauxite was systematically investigated and analyzed through flotation tests. The influence behavior was examined using contact angle measurements, BPWA tests, zeta potential measurements, microscopic analysis, reaction heat, and TOF-SIMS tests. The following conclusions were drawn:

- (1) The main sulfur-containing mineral in the high-sulfur bauxite was pyrite, whereas the main clay minerals were illite and kaolinite. Pyrite, diaspore, illite, and kaolinite were tightly embedded in each other, resulting in the production of high quantities of fine illite and kaolinite particles during the liberation of pyrite or diaspore. Under acidic conditions, the  $\varepsilon_a$  of the kaolinite (or illite)-pyrite pulp was lower than the  $\varepsilon_T$  across all SBX concentrations. However,  $\varepsilon_a$  was significantly higher than  $\varepsilon_T$  under alkaline conditions.
- (2) The iron oxide on the pyrite surface reacted with H<sup>+</sup>, resulting in additional pyrite surface exposure under acidic conditions. SBX was readily chemically adsorbed onto the fresh surface of pyrite, resulting in hydrophobic agglomeration between the pyrite particles and favorable floatability. However, the charge of the kaolinite (or illite) surface was opposite to that of pyrite, and the adsorption of kaolinite (or illite) on the pyrite surface reduced its collecting effect. Kaolinite (or illite) wrapped around pyrite and prevented the adsorption of SBX on its surface. This reduced the surface hydrophobicity of pyrite because of the strong hydrophilic properties of kaolinite (or illite).
- (3) The hydrophilic substance,  $Fe(OH)_2/Fe(OH)_3$ , was formed on the pyrite surface under alkaline conditions. Pyrite and SBX were negatively charged; therefore, their electrostatic repulsion decreased the collection of pyrite by SBX, resulting in a reduction in pyrite floatability. However, substances dissolved from kaolinite (or illite) inhibited the formation of hydrophilic substances on the pyrite surface in the presence of kaolinite (or illite), providing more sites for SBX adsorption on the pyrite surface. In addition, some kaolinite (or illite) particles adsorbed on the surface of pyrite and floated with pyrite, resulting in a higher  $\varepsilon_a$  value for the kaolinite (or illite) -pyrite pulp than that of the  $\varepsilon_T$  under alkaline conditions.

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