Effects of Galvanic Interaction between Chalcopyrite and Monoclinic Pyrrhotite on Their Flotation Separation

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Abstract: The galvanic interaction between chalcopyrite and monoclinic pyrrhotite and its effect on flotation separation were studied using monomineral flotation tests, adsorption capacity tests, X-ray photoelectron spectroscopy (XPS) characterization, and scanning electron microscopy (SEM) test. These results showed that the interaction promoted the reduction of O2 on the cathodic chalcopyrite surface and accelerated the generation of Fe(OH)3, which was not conducive to collector adsorption; hence, the flotation recovery decreased by 10–16%. On the other hand, galvanic interaction accelerated the oxidation of S on the anodic monoclinic pyrrhotite surface to S8 or SO42− and produced a large amount of H+, thus preventing the formation of Fe(OH)3. Meanwhile, the Cu2+ eluted from chalcopyrite surface activated monoclinic pyrrhotite; hence, the flotation recovery increased by 3–10%. Galvanic interaction reduced the floatability difference between the two minerals, and the separation difficulty was significantly increased. Even with an increase in the amount of lime, the separation could not be improved.

Keywords: chalcopyrite; monoclinic pyrrhotite; galvanic interaction; flotation; interactive influence

1. Introduction

Pyrrhotite is a widely distributed pyrite that is often associated with other non-ferrous metal sulfide ores. Pyrrhotite has a variable crystal structure and is easily oxidized and dissolved. These properties make it interfere with the flotation of copper sulfide ore [1–3]. It is often necessary to add a large amount of lime to the slurry to separate copper and sulfur, resulting in low recovery rates of associated metals such as Cu, Au, and Ag, and difficulty in pyrite activation [4–6]. Many researchers have explored the separation process of copper sulfide ores containing pyrrhotite. Luo et al. [7] combined the “copper–lead–zinc priority flotation” process and the zinc–sulfur magnetic separation process to separate a polymetallic sulfide ore containing pyrrhotite, recovering Cu, Pb, and Zn, and effectively separating from sulfur. Zhang [8] used the technological process of “magnetic separation desulfurization–preferential flotation of copper–separation of copper and sulfur–lead flotation from copper tailing–zinc flotation from lead tailing” to select a complex Cu-Pb-Zn ore with high pyrrhotite, and obtained qualified Cu, Pb, and Zn concentrate products. Tong et al. [9] considered the Au-bearing copper ore as an intergrowth with pyrrhotite and used a “mixed flotation–copper sulfur separation–stage grinding and stage separation” technological process combined with highly efficient collector YL-3 to obtain better Cu and Au concentrate indicators. Chen et al. [10] considered the unsatisfactory beneficiation indexes of pyrrhotite copper ore and conducted a series of flotation test studies. The results showed...
that sodium humate can better inhibit pyrrhotite when the pH is 9–10. Zeng et al. [11] studied the flotation separation mechanism of chalcopyrite and pyrrhotite and found that butyl xanthate oxidized on the surface of chalcopyrite to form double xanthate, and lime produced a calcium film on the surface of pyrrhotite to inhibit its redox activity and achieve separation of the two. Khosoo et al. [12] found that the presence of a new harmless reagent (polyglutamic acid, PGA) hindered the electrochemical activity of the collector on the surface of pyrrhotite, inhibiting its flotation. However, most of these studies were process or reagent optimization studies; the inherent reasons for difficulty in separating Cu and S from pyrrhotite are still unclear.

Due to different surface electrostatic potentials, a “galvanic cell” that produces a galvanic effect is formed between the sulfide ores with semiconducting properties when they are in contact during the flotation process [13–15]. In the process, the material with the lower electrostatic potential acts as the anode, whose surface oxidizes and dissolves; and the material with the higher electrostatic potential is inert and acts as the cathode, which is to be protected [16–18]. Galvanic interaction has a significant impact on the surface properties and mineral floatability. The scheme for the interaction is illustrated in Figure 1 [19,20]. This interaction may be an important reason for the difficulty in separating pyrrhotite from copper sulfide ore. Xia et al. [21] found that the galvanic interaction between copper-activated sphalerite and pyrite affected the adsorption of Cu\(^{2+}\) on the surface of pyrite. This helped sphalerite to preferentially adsorb the Cu and suppress the flotation of pyrite. Nakazawa et al. [22] measured the electrostatic potential and galvanic current of pyrite and pyrrhotite mineral electrodes and reported that galvanic electrical contact can improve the floatability of pyrrhotite and reduce pyrite flotation recovery. Through XPS and SEM tests, it was determined that the amount of hydroxide or oxide and iron sulfate on the surface of pyrrhotite decreased when they were in contact with each other, and the amount on the surface of pyrite increased. Miller et al. [23] found that the presence of chalcopyrite promoted the oxidation of xanthate on the surface of pyrrhotite, improving its floatability. Kan [24] studied the flotation law of binary artificial mixed ore composed of pyrrhotite and galena, sphalerite, chalcopyrite, and brittle sulfur antimonite. The results showed that pyrrhotite and galena, sphalerite, chalcopyrite, and brittle antimony led to galvanic electrical contact between these sulfide ores, with a significant impact on their floatability.

Figure 1. Galvanic interaction model of sulfide minerals in sulfide pulp.

In summary, researchers have conducted much research on the influence of pyrrhotite on other sulfide ore flotation processes and indicators, and the interaction between pyrrhotite and pyrite. However, there are few studies on the interaction between pyrrhotite and chalcopyrite, especially the interaction between the flotation processes of different crystal systems of pyrrhotite and chalcopyrite. Thus, in-depth research on the galvanic interaction between pyrrhotite of different crystal systems and chalcopyrite, and the laws that affect their flotation behavior is necessary as a basis for the research and development of a Cu-S low-alkali separation process. Monoclinic pyrrhotite and chalcopyrite are considered as the research objects in this study; the galvanic effects on monoclinic pyrrhotite and chalcopyrite are systematically investigated through monomineral flotation tests, adsorption capacity tests, XPS analysis, SEM, and other research methods. The research results can
provide theoretical guidance for efficient separation of pyrrhotite-bearing copper sulfide ore resources.

2. Materials and Methods

2.1. Samples and Reagents

Chalcopyrite used in the experiment was collected from Daye, Hubei; monoclinic pyrrhotite was obtained from Honggiling, Jilin. They were hand-picked to remove any visible impurities after crushing. The samples were dry-milled using a porcelain ball mill and sieved to obtain a particle size of \(-0.074 \pm 0.038\) mm, placed in a brown wide-mouth bottle, and stored in a refrigerator for flotation. Detailed descriptions of the mineral samples are presented in Table 1. The purities of chalcopyrite and monoclinic pyrrhotite were 95.30\% and 97.70\%, respectively. The X-ray diffraction (XRD) spectra are shown in Figure 2. The XRD pattern of monoclinic pyrrhotite showed a double peak of \(d_{102}\) at \(2\theta = 43.5^\circ\), confirming the presence of monoclinic pyrrhotite [25].

Table 1. Chemical composition of mineral sample (%).

| Mineral             | Fe    | S     | Cu     | Pb    | SiO₂ | CaO | Al₂O₃ |
|---------------------|-------|-------|--------|-------|------|-----|-------|
| Chalcopyrite        | 30.41 | 35.11 | 33.15  | 0.018 | 0.33 | 0.2 | 0.16  |
| Monoclinic pyrrhotite| 58.90 | 38.80 | 0.36   | 0.0068| 0.52 | 0.23| 0.16  |

Figure 2. XRD patterns of (a) chalcopyrite; (b) monoclinic pyrrhotite.

Sodium hydroxide (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), hydrochloric acid (Sinopharm Chemical Reagent Co., Ltd., China), calcium oxide (Sinopharm Chemical Reagent Co., Ltd., China), and methyl isobutyl carbinol (MIBC) (Xilong Chemical Co., Ltd., Shantou, China) used in the test were all analytically pure. Butyl xanthate (Zhuzhou Mineral Processing Pharmacy Factory, Hunan, China) was purified by acetone and petroleum ether; deionised water was used as the test water.

2.2. Research Methods

2.2.1. Monomineral Flotation Test

Monomineral flotation tests were conducted in a 40 mL plexiglass tank in the XFG-II flotation machine (Jilin Prospecting Machinery Factory, Changchun, China). Before the flotation test, 2 g of monomineral was cleaned with an ultrasonic cleaner for 5 min and allowed to stand for 2 min. The supernatant was poured out and the mineral sample was rinsed into the flotation tank with deionised water. According to the test requirements, pH adjusters, inhibitors, collectors, and foaming agents were sequentially added to the slurry for the flotation tests. The obtained foam product and the product in the tank were filtered, dried, and weighed, and the flotation recovery was calculated. All tests were conducted
three times. Each data point and error bar represented the average value and standard deviation, respectively.

2.2.2. Adsorption Capacity Test

Butyl xanthate (0.5 g) was weighed and dissolved in deionised water; the volume was fixed in a volumetric flask of volume 500 mL to obtain a 1 g/L xanthate solution. The prepared solution was diluted to obtain butyl xanthate solutions with different concentrations. Their absorbance was measured at a characteristic wavelength of 302 nm; the data were linearly fitted to obtain the standard curve for the butyl xanthate solution. Next, 0.5 g of pure mineral and 10 mL of deionized water was added to a 50 mL Erlenmeyer flask and the pH was adjusted with hydrochloric acid and sodium hydroxide. The xanthate solution was also added to the flask and it was sealed with plastic wrap and a rubber band. The flask was then stirred, allowed to stand, and centrifuged. The supernatant was extracted, and the absorbance was measured again. Each point was conducted three times. The data point and error bar represented the average value and standard deviation, respectively. The adsorption capacity was calculated using the following formula:

$$Q_t = \frac{(c_0 - c_t)V}{W}$$

where $c_0$ is the initial concentration of the butyl xanthate solution (mg/L); $c_t$ is the butyl xanthate concentration of the supernatant at time $t$ (mg/L); $W$ is the weight of pure mineral (g); $V$ is the volume of butyl xanthate solution (L); the corresponding adsorption capacity is $Q_t$ (mg/g).

2.2.3. Cu$^{2+}$ Dissolution Test

A sample of chalcopyrite (3 g) and different amounts of monoclinic pyrrhotite (0 g, 0.5 g, 1 g, 2 g, and 3 g) were added to 15 mL of deionized water and stirred at 500 rpm for 20 min at 25 °C. The pulp was quickly filtered using a syringe to collect the solution sample. All solution samples were analyzed using atomic absorption spectroscopy to measure the concentration of Cu$^{2+}$. All tests were conducted three times to determine the average value and standard deviation.

2.2.4. XPS Test

The X-ray photoelectron spectrometer (K-Alpha + device, Thermo Scientific, Waltham, MA, USA) was used for XPS analysis. The vacuum degree of the analysis chamber was $\sim 5 \times 10^{-9}$ mbar; the X-ray source was a monochromatic AlKα source (Mono AlKa), and the working voltage was 15 kV. A sample (2 g) was weighed and placed in a vacuum drying oven at 40 °C. The sample was pressed into a thin sheet with an abrasive tool, and XPS analysis was performed.

2.2.5. SEM Test

Chalcopyrite was cleaned with deionized water in an ultrasonic cleaner for 5 min and allowed to stand for 2 min to extract the supernatant. A part of the sample was directly placed in a vacuum drying oven at 40 °C; the remainder of the sample was mixed with monoclinic pyrrhotite, stirred in deionized water for 20 min, filtered, and dried at 40 °C in a vacuum. A Zeiss Sigma 300 SEM was used to observe the changes in the surface microstructure of chalcopyrite before and after galvanic interaction with monoclinic pyrrhotite.

3. Results and Discussion

3.1. Influence of Galvanic Interaction on Flotation Behavior of Chalcopyrite and Monoclinic Pyrrhotite

The effects of butyl xanthate, pulp pH, and lime on the flotation behavior of chalcopyrite and monoclinic pyrrhotite before and after galvanic interaction were investigated in
3.1. Influence of Butyl Xanthate Dosage on Flotation Behavior of Chalcopyrite and Monoclinic Pyrrhotite

In natural pH conditions (pH = 6.56) and a foaming agent (MIBC) dosage of 15 mg/L, the effect of the dosage of collector butyl xanthate on the flotation behavior of chalcopyrite and monoclinic pyrrhotite before and after galvanic interaction was investigated. The test results are presented in Figure 3.

![Figure 3. Influence of butyl xanthate dosage on flotation behavior of chalcopyrite and monoclinic pyrrhotite before and after galvanic interaction. (x-axis butyl xanthate dosage starts from 0 mg/L, y-axis recovery starts from 50%).](image)

From Figure 3, the flotation recovery of chalcopyrite and monoclinic pyrrhotite increased with an increase in the butyl xanthate dosage. The mineral flotation recovery tended to peak when the concentration reached 15 mg/L. Thus, 15 mg/L butyl xanthate was determined to be the best dosage.

The interaction between chalcopyrite and monoclinic pyrrhotite formed a galvanic cell. With a higher electrostatic potential on the surface, chalcopyrite acted as the cathode [26]. O₂ caused a reduction reaction on its surface, which accelerated the generation of hydrophilic substances and reduced floatability. The flotation recovery decreased by 11%–14% compared with the recovery before galvanic interaction, as shown in Figure 3. The surface electrostatic potential of monoclinic pyrrhotite was lower and it acted as the anode of the galvanic cell. The following oxidation reactions may occur on the surface [27].

\[
\text{FeS} + 4\text{H}_2\text{O} = \text{Fe}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e}^-
\]

The presence of H⁺ inhibited the formation of hydrophilic substances such as Fe(OH)₃ on the surface of monoclinic pyrrhotite and the floatability was enhanced. The recovery increased by 8%–10% compared with the recovery before galvanic interaction.

3.1.2. Influence of Pulp pH on Flotation Behavior of Chalcopyrite and Monoclinic Pyrrhotite

Using hydrochloric acid and sodium hydroxide as the pulp pH adjusters, with 15 mg/L butyl xanthate and 15 mg/L MIBC, the effect of different pulp pH values on the flotation...
behavior of chalcopyrite and monoclinic pyrrhotite before and after galvanic interaction was investigated. The test results are presented in Figure 4.

![Figure 4](image-url)

**Figure 4.** Influence of pulp pH on flotation behavior of chalcopyrite and monoclinic pyrrhotite before and after galvanic interaction. (x-axis pH starts from 4, y-axis recovery starts from 10%).

From Figure 4, before galvanic interaction, the floatability of chalcopyrite was better than that of monoclinic pyrrhotite in the investigated pH range; its flotation recovery was generally greater than 90% and less affected by pH. The flotation recovery of monoclinic pyrrhotite first increased and then decreased with an increase in pH; the floatability was best in a weakly alkaline range (pH = 8–10). After galvanic interaction, the flotation recovery of chalcopyrite decreased by 10%–16%, and the recovery of monoclinic pyrrhotite increased by 3%–10%, as shown in Figure 4. When the pH was higher than 5, the recovery of monoclinic pyrrhotite was better than that of chalcopyrite, possibly because a neutral to alkaline solution is more conducive to formation of hydrophilic substances such as Fe(OH)$_3$ on the chalcopyrite surface. The galvanic interaction significantly reduced the difference in floatability between the two minerals; at pH = 12, the difference in flotation recovery between the two was reduced from 15.15% before interaction to 7.09%. When pH = 4, the maximum difference was seen.

3.1.3. Influence of Lime Dosage on Flotation Behavior of Chalcopyrite and Monoclinic Pyrrhotite

In natural pH conditions (pH = 6.56), with 15 mg/L butyl xanthate and 15 mg/L MIBC, monomineral flotation tests were performed with lime as an inhibitor. The influence of lime dosage on the flotation behavior of chalcopyrite and monoclinic pyrrhotite before and after galvanic interaction was investigated. The test results are presented in Figure 5.

Figure 5 shows that lime had no inhibitory effect on chalcopyrite but had a certain inhibitory effect on monoclinic pyrrhotite. The floatability of monoclinic pyrrhotite before and after galvanic interaction tended to decrease with an increase in lime consumption; the recovery decreased by 5% and 10%, respectively. Consistent with the laws shown in Figures 3 and 4, the galvanic interaction between the two minerals reduced the recovery of chalcopyrite by 3%–6%; the recovery of monoclinic pyrrhotite increased by 4%–8%. When the lime dosage was low, the difference in floatability was small. The difference between the flotation recovery of the two minerals did not reach the maximum until the lime dosage increased to $2.5 \times 10^{-3}$ mol/L, the difference before galvanic interaction was 12.56%, and the value after galvanic interaction was reduced to 5.17%. It was difficult to separate chalcopyrite and monoclinic pyrrhotite after galvanic interaction even with a large amount of lime.
Figure 5. Influence of lime dosage on flotation behavior of chalcopyrite and monoclinic pyrrhotite before and after galvanic interaction. (x-axis lime dosage starts from 0 mol/L, y-axis recovery starts from 50%).

3.2. Analysis of Reagent Adsorption Capacity on Mineral Surface

The difficulty of the collector to act on the target mineral surface is the key to controlling the mineral flotation index. To investigate the effect of galvanic interaction between chalcopyrite and monoclinic pyrrhotite on the adsorption capacity of the collector on both surfaces, the butyl xanthate dosage adsorbed on the surface of chalcopyrite and monoclinic pyrrhotite in different pH conditions before and after galvanic interaction was measured with an ultraviolet spectrophotometer. The test results are presented in Figure 6.

Figure 6. Adsorption dosage of butyl xanthate on surface of (a) chalcopyrite and (b) monoclinic pyrrhotite with different pulp pH. (x-axis pH starts from 6).

It is observed in Figure 6a that in the investigated pH range, the change in trend of the adsorption dosage of butyl xanthate on the surface of chalcopyrite was the same before and after galvanic interaction, with a trend of first increasing and then decreasing, with a peak in the pH range of 8–10. After galvanic interaction, the adsorption of butyl xanthate by chalcopyrite decreased over the entire pH range, and the adsorption of butyl xanthate...
by monoclinic pyrrhotite increased slightly (Figure 6b), which was consistent with the flotation test results.

3.3. Analysis of Dissolution of Cu$^{2+}$ on Chalcopyrite Surface

In aqueous solution, some Cu$^{2+}$ is inevitably dissolved from the chalcopyrite surface, and is a good activator of pyrite, pyrrhotite, and other pyrites. In the flotation system of chalcopyrite and monoclinic pyrrhotite, the galvanic interaction between them may have an important influence on the dissolution of Cu$^{2+}$ on the chalcopyrite surface. The effects of different proportions of chalcopyrite and monoclinic pyrrhotite on the dissolution of Cu$^{2+}$ from the chalcopyrite surface were investigated. The test results are presented in Figure 7.

![Figure 7](image.png)

**Figure 7.** Cu$^{2+}$ dissolution from chalcopyrite with different monoclinic pyrrhotite additions. (y-axis concentration of Cu$^{2+}$ starts from 60 mg/L).

Figure 7 shows that without monoclinic pyrrhotite, a large amount of Cu$^{2+}$ (123.77 mg/L) was dissolved from chalcopyrite surface. The addition of monoclinic pyrrhotite inhibited the dissolution of Cu$^{2+}$ from the chalcopyrite surface to some extent. With an increase in monoclinic pyrrhotite content, the inhibitory effect became more obvious. This may be due to the galvanic interaction between chalcopyrite and monoclinic pyrrhotite. Chalcopyrite was protected as a cathode, which slightly weakened its surface dissolution. However, the interaction between the two minerals cannot completely inhibit the dissolution of Cu$^{2+}$ from the chalcopyrite surface. When the mass ratio of the two minerals was 1:1, the Cu$^{2+}$ concentration in the slurry solution was still as high as 80.90 mg/L.

3.4. XPS Analysis of Mineral Surface

To reveal the influence mechanism of the galvanic interaction between chalcopyrite and monoclinic pyrrhotite on their surface properties, XPS tests were conducted on the surface of chalcopyrite and monoclinic pyrrhotite before and after galvanic interaction. The full-spectrum scan spectra of chalcopyrite and monoclinic pyrrhotite are shown in Figure 8a,b. The changes in the surface element concentration and atomic ratio of chalcopyrite and monoclinic pyrrhotite before and after galvanic interaction were investigated; the results are shown in Table 2.
Figure 7 shows that without monoclinic pyrrhotite, a large amount of pyrite and monoclinic pyrrhotite before and after interaction, it is observed that after galvanic interaction with chalcopyrite, there is no change in the elements on the chalcopyrite surface. In Figure 8a, comparing the full-spectrum scan lines of monoclinic pyrrhotite before and after interaction with chalcopyrite, it is observed that after galvanic interaction with chalcopyrite, the monoclinic pyrrhotite surface was electronically bound to a new Cu 2p peak near 931 eV. This indicates that Cu²⁺ dissolved from the chalcopyrite surface was adsorbed on the monoclinic pyrrhotite surface.

From Table 2, after the galvanic interaction of chalcopyrite and monoclinic pyrrhotite, the concentration of elements on the chalcopyrite surface increased in varying degrees; the concentration of Fe increased significantly, and the ratio of Fe/Cu increased from 0.81 to 1.04, without significant changes in the S/Cu ratio. This was attributed to the dissolution of the chalcopyrite surface and the galvanic interaction that caused O₂ to undergo a reduction reaction on the chalcopyrite surface to generate OH⁻. This led to the formation of hydrophilic Fe(OH)₃, which adhered to the chalcopyrite surface and increased its hydrophobicity. After galvanic interaction, the relative content of S on the monoclinic pyrrhotite surface increased slightly, indicating a S-rich state. The Cu concentration detected on the surface was 3.62%, which is consistent with the result shown in Figure 8b. This may be an important reason for the improved floatability of monoclinic pyrrhotite after galvanic interaction.

3.5. SEM Analysis of Mineral Surface Topography

To determine the influence of the galvanic interaction between monoclinic pyrrhotite and chalcopyrite on the surface properties of chalcopyrite, SEM tests were conducted on the chalcopyrite surface before and after galvanic interaction. The results are shown in Figure 9a,b.
From Table 2, after the galvanic interaction of chalcopyrite and monoclinic pyrrhotite, the chalcopyrite surface was smoother. After interaction, the overall surface appearance was rougher and a lot of flocculent substances were produced on the surface. Combined with the analysis of the changes in the concentration of elements on the surface of chalcopyrite in Table 2, this was attributed to accelerated formation of Fe(OH)$_3$ deposits on the chalcopyrite surface after galvanic interaction.

4. Conclusions

(1) The monomineral flotation behaviors of chalcopyrite and monoclinic pyrrhotite before and after galvanic interaction were investigated. The results showed that the interaction between chalcopyrite and monoclinic pyrrhotite in the solution formed a galvanic cell, and galvanic interaction occurred. In the monomineral flotation system, chalcopyrite and monoclinic pyrrhotite exhibited a large difference in floatability and were easier to separate. In the mixed system of two minerals, the flotation recovery of chalcopyrite decreased due to galvanic interaction, and the flotation recovery of monoclinic pyrrhotite increased. The difference in floatability between the two minerals was significantly reduced. Effective separation could not be achieved, even with an increased lime dosage.

(2) The results of the adsorption capacity test, Cu$^{2+}$ dissolution test, XPS, and SEM analysis showed that chalcopyrite and monoclinic pyrrhotite in the solution contacted each other and produced a galvanic interaction. The interaction caused the cathodic chalcopyrite surface to accelerate the formation of hydrophilic substances such as Fe(OH)$_3$, which reduced the hydrophobicity of the chalcopyrite surface and the adsorption capacity for butyl xanthate. Galvanic interaction accelerated the oxidation of S on the anode monoclinic pyrrhotite surface to S$\,_{\text{O}}$ or SO$_4^{2-}$ and produced a large amount of H$^+$, preventing formation of hydrophilic substances such as Fe(OH)$_3$. Meanwhile, the Cu$^{2+}$ eluted from the chalcopyrite surface activated the monoclinic pyrrhotite and promoted the adsorption of butyl xanthate.

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As shown in Figure 9, before interaction with monoclinic pyrrhotite, the chalcopyrite surface was smoother. After interaction, the overall surface appearance was rougher and a lot of flocculent substances were produced on the surface. Combined with the analysis of the changes in the concentration of elements on the surface of chalcopyrite in Table 2, this was attributed to accelerated formation of Fe(OH)$_3$ deposits on the chalcopyrite surface after galvanic interaction.
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References
1. He, M.; Qin, M.; Li, W.; Jiao, F. Flotation performances of polymorphic pyrrhotite. J. Cent. South Univ. 2016, 19, 238–243. [CrossRef]
2. Fuerstenau, M.C.; Sabacky, B.J. On the natural floatability of sulfides. Int. J. Miner. Process. 1981, 8, 79–84. [CrossRef]
3. Janzen, M.P.; Nicholson, R.V.; Sharrer, J.M. Pyrrhotite reaction kinetics: Reaction rates for oxidation by oxygen, ferric iron, and for nonoxidative dissolution. Geochim. Cosmochim. Acta 2000, 64, 1511–1522. [CrossRef]
4. Tegin, I.; Ziyadanogullari, R. The effect of sulfurization process on flotation of copper ore containing gold and silver. J. Miner. Mater. Charact. Eng. 2008, 7, 193–202. [CrossRef]
5. Mustafa, S.; Hamid, A.; Naeem, A. Xanthate adsorption studies on chalcopyrite ore. Int. J. Miner. Process. 2005, 74, 317–325. [CrossRef]
6. Nadeif, A.; Taha, Y.; Bouzahzah, H. Desulfurization of the old tailings at the Au-Ag-Cu tiouit mine. Minerals 2019, 9, 401. [CrossRef]
7. Luo, X.; Gao, L.; Ma, P.; Han, T.; Yan, Q. Studies on beneficiation process for copper-lead-zinc polymetallic sulphide ore in Anhui. Nonferrous Met. Miner. Processing Part 2014, 5, 34.
8. Zhang, T. Beneficiation separation experiment on a high-pyrrhotite copper-lead-zinc ore. Sichuan Nonferrous Met. 2016, 2, 21. (In Chinese)
9. Tong, X.; Wang, X.; Deng, Z. Research on Au-bearing copper ore in flotation from Yunnan. Front. Manuf. Des Sci. 2014, 496–500, 410–413. [CrossRef]
10. Chen, J.; Li, Y.; Chen, Y. Cu-S flotation separation via the combination of sodium humate and lime in a low pH medium. Miner. Eng. 2011, 24, 58–63. [CrossRef]
11. Zeng, W.; Ren, L.; Cao, Y.; Zeng, S. Study on mechanism of action of xanthate in flotation separation of chalcopyrite and pyrrhotite. Nonferrous Met. Miner. Processing Part 2020, 6, 30–35.
12. Khoso, S.A.; Gao, Z.; Meng, X. The depression and adsorption mechanism of polyglutamic acid on chalcopyrite and pyrrhotite flotation systems. Minerals 2019, 9, 510. [CrossRef]
13. Feng, Q. Galvanic corrosion in sulphide ore slurry system and its influence on flotation (II): The influence of galvanic corrosion on the loss of grinding media and the flotation of sulfide minerals. Met. Min. Process. Abroad 1999, 9, 5–8.
14. Qin, W.; Wang, X.; Ma, L.; Jiao, F.; Liu, R.; Gao, K. Effects of galvanic interaction between galena and pyrite on their flotation in the presence of butyl xanthate. Trans. Nonferrous Met. Soc. China 2015, 25, 3111–3118. [CrossRef]
15. Nowak, P.; Krauss, E.; Pomianowski, A. The electrochemical characteristics of the galvanic corrosion of sulphide minerals in short-circuited model galvanic cells. Hydrometallurgy 1984, 12, 95–110. [CrossRef]
16. Ekmeqi, Z.; Demirel, H. Effects of galvanic interaction on collectorless flotation behavior of chalcopyrite and pyrite. Int. J. Miner. Process. 1997, 52, 31–48. [CrossRef]
17. Owusu, C.; Addia-Mensah, J.; Fornasiero, D.; Zanin, M. Estimating the electrochemical reactivity of pyrite ores—their impact on pulp chemistry and chalcopyrite flotation behaviour. Adv. Powder Technol. 2013, 24, 801–809. [CrossRef]
18. Liu, Q.; Li, H.; Zhou, L. Galvanic interactions between metal sulfide minerals in a flowing system: Implications for mines environmental restoration. Appl. Geochem. 2008, 23, 2316–2323. [CrossRef]
19. Liu, D.; Zhang, G.; Liu, J.; Pan, G.; Chen, Y.; Wang, M. Studies on the surface oxidation and its role in the flotation of mixed Cu-Ni sulfide ore. Powder Technol. 2021, 381, 576–584. [CrossRef]
20. Wang, X.; Qin, W.; Jiao, F.; Wu, J. The influence of galvanic interaction on the dissolution and surface composition of galena and pyrite in flotation system. Miner. Eng. 2020, 156, 106525. [CrossRef]
21. Xia, L.; Hart, B.; Larachi, F.; Gravel, O. Galvanic interaction of pyrite with Cu activated sphalerite and its effect on xanthate adsorption. Can. J. Chem. Eng. 2019, 97, 2671–2677. [CrossRef]
22. Nakazawa, H.; Iwasaki, J. Effect of pyrite-pyrrhotite contact on their floatabilities. Miner. Metall. Process. 1985, 2, 206–221. [CrossRef]
23. Miller, J.D.; Li, J.; Davidtz, J.C.; Vos, F. A review of pyrrhotite flotation chemistry in the processing of PGM ores. Miner. Eng. 2005, 18, 855–865. [CrossRef]
24. Kang, D. Galvanic Effect on the Flotation Behavior of Sulfide Minerals and Its Influence on the Electronic Structure and Properties. Master’s Thesis, Guangxi University, Nanning, China, 2014.
25. Hong, Q. Study on the Crystal Chemistry and Floatability of Pyrrhotite. Master’s Thesis, Central South University, Changsha, China, 2011.
26. Payant, R.; Rosenblum, F.; Nesset, J.E.; Finch, J.A. The self-heating of sulfides: Galvanic effects. Miner. Eng. 2012, 26, 57–63. [CrossRef]
27. Cheng, X.; Iwasaki, I. Effect of chalcopyrite and pyrrhotite interaction on flotation separation. Min. Metall. Explor. 1992, 9, 73–79. [CrossRef]