

Depressant-free flotation separation of chalcopyrite and galena by surface oxidation pretreatment: Effect of applying potassium peroxymonosulfate as a novel and efficient oxidant

Hepeng Zhou ^{1,2}, Jiangfeng Guo ^{1,2}, Guangjie Zhu ^{1,2}, Hao Xu ^{1,2}, Xuekun Tang ^{1,2}, Xianping Luo ^{1,2}

¹ Jiangxi Province Key Laboratory of Mining and Metallurgy Environmental Pollution Control, Jiangxi University of Science and Technology, Ganzhou 341000, China

² Faculty of Resource and Environmental Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

Corresponding author: txk0797@126.com (Xuekun Tang)

Abstract: The flotation separation of chalcopyrite and galena presents significant challenges due to their similar surface properties, resulting in comparable floatability. In the process of flotation separation, conventional depressants encounter issues related to high toxicity or limited effectiveness. In this paper, it was found that the floatability of galena decreased significantly after pretreatment with potassium peroxymonosulfate (PMS) oxidation. The influence on chalcopyrite, however, is relatively insignificant. In flotation tests of mixed binary minerals, without PMS oxidation, the two minerals are basically floating; When the pH is 8 and the dosage of PMS is 0.375 g/L, it is possible to obtain a flotation concentrate with a Pb grade of 26.78% and recovery of 36.10%, as well as a Cu grade of 21.53% and recovery of 83.66%, when the raw ore contains Pb 44.88% and Cu 15.57%. The oxidation pretreatment method enables the separation of galena and chalcopyrite without the need for a depressant. The XPS and AFM measurements revealed a significantly higher oxidation degree of galena compared to chalcopyrite after treatment with PMS, indicating a notable difference in their floatability. Consequently, the separation of chalcopyrite and galena is greatly facilitated by this distinction. In conclusion, PMS can be considered as a novel oxidant that provides an effective approach for selectively floating chalcopyrite and galena.

Keywords: chalcopyrite, galena, potassium peroxymonosulfate, selective oxidation, flotation separation

1. Introduction

Copper, as an important non-ferrous metal, is widely used in various fields of production and life, and plays an important role in the national economy (Zhang et al., 2020; Wei et al., 2019). Chalcopyrite, the most common and widely distributed copper-bearing mineral, is the main source of copper extraction in the industry (Miao et al., 2022; Liu et al., 1989). It occurs naturally as polymetallic sulfide deposits, where copper-lead sulfide deposits are the most prevalent. It is often related to galena in the ore (Yang et al., 2023). The chalcopyrite is a typical naturally hydrophobic sulfide ore. Currently, in the industry, froth flotation is the primary method employed for the comprehensive recovery of chalcopyrite. Froth flotation is a physicochemical technique that exploits varying surface hydrophobic properties among different minerals (Huang et al., 2014; Liu et al., 2000). However, galena is also a sulfide ore and exhibits similar surface properties to chalcopyrite, thereby resulting in their analogous floatability. Consequently, achieving efficient separation of chalcopyrite and galena becomes quite challenging in the flotation process (Zhu et al., 2022). The inadequate quality of copper concentrate often results in complications during the subsequent smelting process, leading to increased production costs and other issues. In industrial chalcopyrite mineral processing plants, the effectiveness of Cu-Pb separation is

widely regarded as one of the most crucial indicators (Tang et al., 2019; Zhang et al., 2019; Su et al., 2022a; Zhang et al., 2022a).

The distinction between chalcopyrite and galena has been extensively studied, with significant progress made thus far. The prevailing approach involves the application of depressants to selectively impede the flotation of galena. (Rath. RK et al., 2022). For a long time, potassium dichromate, as the most widely used inhibitor in industry, can selectively reduce the floatability of galena. However, the high toxicity of this kind of reagent restricted its further application. To conquer the problem, low-toxicity depressants, e.g. sodium sulfide, sodium hydrosulfide, and sodium sulfite, were also developed for flotation separation of galena and chalcopyrite (Zhang et al., 2022b; Huang et al., 2012; Mu et al., 2016; Yang et al., 2020). However, the selectivity of this type of reagent is suboptimal, which may also have a detrimental impact on the recovery of chalcopyrite. Additionally, macromolecular organics such as dextrin, locust bean gum, and other natural polymers are introduced as depressants; nevertheless, these reagents also suffer from the notable drawback of poor solubility and high consumption (Cao et al., 2006). In addition, an excess of these inhibitors would increase the COD (chemical oxygen demand) concentration of wastewater, bringing extra environmental pressure.

Apart from the addition of a depressant, the selective oxidation method is a potential alternative and is considered an eco-friendly way that can be applied in the flotation separation of sulfide ore. In our previous research (Yang et al., 2022), we found that the selective oxidation of galena can be realized via thermal pretreatment. However, the high costs associated with thermal pretreatment significantly restrict its practical application. The utilization of oxidants in the pulp has been investigated as a more cost-effective means to achieve mineral surface oxidation (Hirajima. T et al., 2017; Suyantara. GPW et al., 2018a; Lei et al., 2023). The key factor for achieving selective oxidation of galena lies in the choice of oxidant. However, commonly employed oxidants such as hydrogen peroxide, sodium hypochlorite, and potassium permanganate all exhibit poor selectivity (Yi et al., 2021; Suyantara. GPW et al., 2018b; Yang et al., 2016), a finding that has also been confirmed in our preliminary experiment. Despite encountering various challenges, the surface oxidant method still holds promise for the flotation separation of Cu-Pb.

In addition to the aforementioned well-known oxidants, potassium peroxydisulfate (PMS) is also a highly efficient and viable oxidant, making it a potentially exceptional reagent for application in the flotation separation of chalcopyrite and galena. The active substance of composite salt PMS is potassium bisulfate KHSO_5 , which can be used as an oxidant, bleach, catalyst, disinfectant, etching agent, and so on. It has the characteristics of a broad spectrum, high efficiency, and low toxicity. In the PMS oxidation system, hydroxyl radicals ($E=1.9\text{-}2.7\text{ V}$) and sulfate radicals ($E_0=2.5\text{-}3.1\text{ V}$) with high oxidative potential can also be generated, which can further enhance the oxidation effect (Tang et al., 2018). In exploratory experiments, we found PMS can selectively oxidize the surface of galena but barely influence the flotation of chalcopyrite.

Therefore, this paper aims to utilize PMS as a novel oxidizing agent for the pretreatment of galena and chalcopyrite in order to achieve selective oxidation. This approach seeks to enhance the disparities in surface properties between galena and chalcopyrite, thereby significantly differentiating their floatability. In this study, separate pre-oxidation-single mineral flotation tests and pre-oxidation-mixed ore flotation tests were conducted on chalcopyrite and galena respectively. The flotation test phenomena were examined to investigate the oxidative effect of PMS. Through XPS and ESR testing methods, the selective oxidation mechanism of PMS on both minerals was analyzed, providing essential theoretical support for subsequent efficient regulation of flotation behavior.

2. Experimental

2.1. Sample preparation and reagents

The high-purity chalcopyrite and galena samples used as raw materials in this experiment are both bulk samples from Hunan Province, China. The samples were first manually broken into small pieces and selected, and then ground into dry powder by a three-head agate grinder. The 200-mesh and 400-mesh standard Taylor screens were used for dry screening to obtain a mineral powder with a particle size of $-0.074\text{ mm}+0.037\text{ mm}$, which was respectively put into bags and sealed for storage to prevent further oxidation of the surface of sulfide ore.

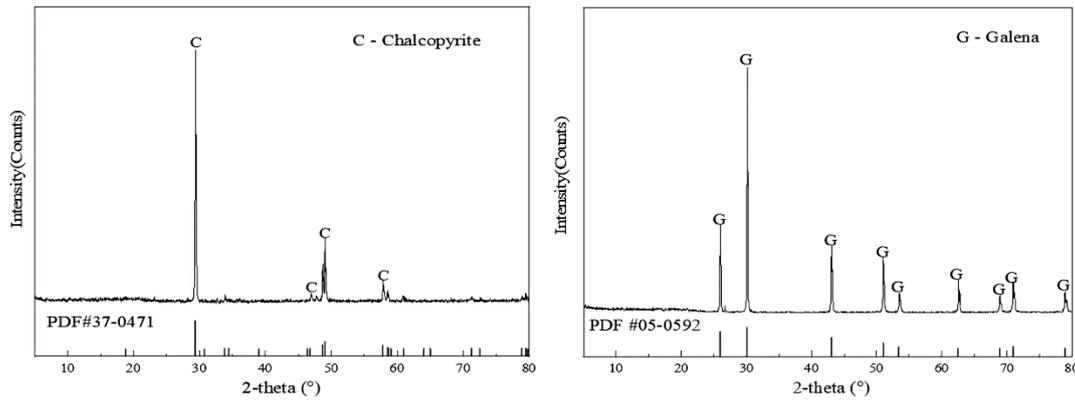


Fig. 1. XRD patterns of the as-prepared mineral samples of Chalcopyrite and Galena.

Table 1. Chemical composition of chalcopyrite and galena (%)

Sample	Cu	Pb	Zn	S	Fe	CaO	MgO	SiO ₂	Al ₂ O ₃
Chalcopyrite	32.83	0.23	0.45	34.02	28.88	0.51	0.34	0.66	0.27
Galena	—	83.56	0.26	12.55	0.28	0.31	0.12	0.45	0.15

As shown in Fig. 1 and Table 1, the results of XRD and chemical composition analyzes show that the quality of these two minerals with purities of approximately 95% and 96% for chalcopyrite and galena, respectively. The chalcopyrite and galena in the samples used have low impurity content and high purity, which meet the requirements of pure mineral experimental research.

The oxidants PMS, H₂O₂, and NaClO used in the pre-oxidation process were from Shanghai Macklin Biochemical Co., Ltd., both of which belong to the analytical pure level. In the flotation process, sodium hydroxide (AR grade) and hydrochloric acid (AR grade) were used to adjust the pH of the pulp, and butyl xanthate (SBX) from the analytical pure grade was used to enrich and collect minerals. Deionized water was used throughout the test and detection process.

2.2. Experimental procedure

2.2.1. PMS oxidation pretreatment

PMS oxidation pretreatment of mineral samples is relatively simple. During each oxidation pretreatment process, a 2 g sample, the proper amount of PMS, and 35 ml of deionized water were accurately weighed in a small beaker of 100 ml, which was placed in a magnetic stirrup and stirred with a rotor for 15 min. At the end of stirring, remove the rotor, let it stand for 10 min so that the mineral precipitates in the lower layer, and pour out the upper liquid. In the oxidation pretreatment of mixed minerals, chalcopyrite and galena with a 1:1 mass ratio were used to prepare mineral samples. Other operations were the same as those for a single mineral.

2.2.2 Micro-flotation tests

The flotation operations are all carried out at room temperature (about 25 °C) in the same hanging flotation machine, which is equipped with a small chamber (volume: 40 ml) and the impeller speed is fixed at 1900 RPM throughout the flotation process. For a single mineral, the pre-oxidized 2 g sample and 35 ml deionized water were mixed into the flotation tank first, and the slurry was adjusted for 2 min to form a uniform slurry. At the same time, NaOH solution or HCl solution was used for pH adjustment. After 3 min, a certain amount of collector butyl xanthate was added for 5 min. Then, the baffle was put in for aeration and flotation, and the floating foam products in the upper layer were manually collected as a concentrate in the clean and dry glass dish, and the bubble scraping time was 3 min. The upper concentrate product and bottom tailings product are dried and weighed successively.

The flotation recovery rate can be calculated according to formula (1) (where R represents the recovery rate; W_c and W_t represent the weight of concentrate and tailings, respectively).

$$R = \frac{W_c}{W_c + W_t} \cdot 100\% \quad (1)$$

For the flotation results of mixed minerals, the flotation recovery rate can be calculated according to formula (2) (where C_c and C_m represent the grade of concentrate and mixed ore sample respectively; The other symbols are the same as formula (1)).

$$R = \frac{W_c \cdot C_c}{2 \cdot C_m} \cdot 100\% \quad (2)$$

2.3. Contact angle test

Contact Angle tests were conducted to evaluate the hydrophobic properties of mineral surfaces. The contact angle of chalcopyrite and galena was measured using the KRUSS contact angle measuring instrument (German DSA100). Regularly shaped chalcopyrite and galena samples were selected from raw ore, cut into smooth slices, and polished successively with increasingly fine sandpaper. The same reagent addition sequence was employed for both the contact angle test and micro-flotation test. Each measurement was repeated three times, and the average value was taken as the result.

2.4. Ion concentration detection

Ion concentration detection by testing solution contained in the purpose of varying concentrations of ions can visually analyze changes in chemical composition in the solution. In this paper, the preparation method of the sample for ion concentration detection is as follows: using the PMS dosage conditions set in the micro-flotation test, chalcopyrite and galena are oxidized with different dosages of PMS. For each sample preparation, 2 g of chalcopyrite (galena) was put into a 100ml beaker, 40 ml of deionized water was added, a rotor was placed, and the rotor was stirred on a magnetic stirrer for 15 min and adjusted to pH=8. After stirring, remove the rotor, stand for 10 min, and take the supernatant into the sealed sample bottle for testing.

2.5. XPS measurement

X-ray photoelectron spectroscopy (XPS) is mainly used to measure the binding energy of electrons, which is an effective way to study the chemical composition and state of surface elements. In this test, a Thermo SCIENTIFIC ESCALAB 250xi X-ray photoelectron spectrometer with monochromatic Al K α X-ray source was used to analyze and test the samples, and then Avantage software was used to fit the X-ray photoelectron spectra of specific elements. All binding energies were calibrated using contaminant carbon (C1 s =284.8 eV).

Sample preparation process: Take 2 g pure mineral in 100mL beaker, add the appropriate amount of deionized water, and clean with ultrasonic cleaner 2~3 times, add the appropriate amount of deionized water and add agents according to the optimal reagent system for stirring, at the end of stirring, the solution will stand and pour out the supernatant, and the solid precipitate at the bottom of the beaker will be placed in a vacuum drying oven at 50 °C for drying, that is, the sample for detection will be obtained.

2.6. ESR measurement

Free radical reactions play an important role in chemistry, which can react with the oxidation and reduction of an atom or molecule. Electron spin resonance (ESR) is one of the most direct and effective ways to detect the generation of free radicals and capture the structure of free radicals.

2.7. AFM measurement

The atomic force microscope (AFM) can detect the appearance of the sample from three dimensions and measure its surface roughness. In this paper, the NX10 model machine is used for AFM detection. During sample preparation, the mineral samples are first polished, then soaked with different agents, and the mineral surface is dried by nitrogen injection and then tested.

3. Results and discussion

3.1. Micro-flotation results

To evaluate the oxidation effect of PMS on chalcopyrite and galena, a single mineral flotation condition test was carried out, and the influences of four factors including the dosage of PMS, oxidation time, flotation pH value, and dosage of sodium butyl xanthate (SBX) during the oxidation pretreatment before flotation were investigated respectively. For comparative purposes, hydrogen peroxide (H_2O_2) and sodium hypochlorite ($NaClO$) were also tested as oxidants in the flotation test. Each condition was repeated three times.

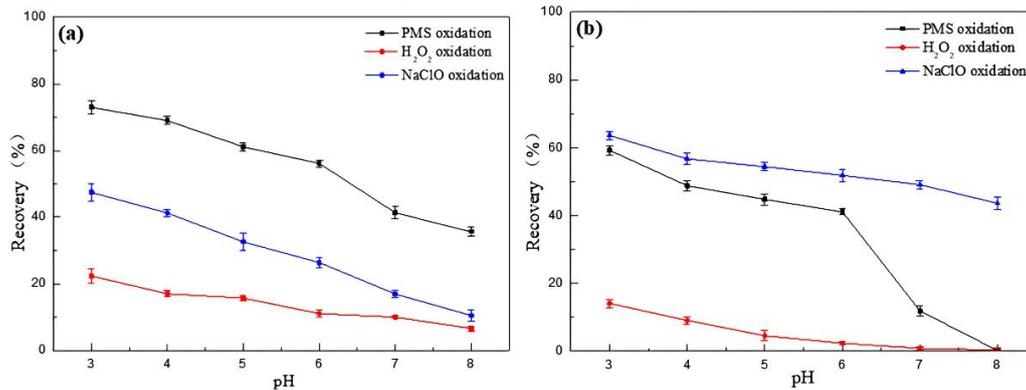


Fig. 2 Effects of pH values on flotation recovery of chalcopyrite (a) and galena (b) pretreated under different oxidation pretreatment systems

Fig. 2 shows the effect of flotation pH value on the flotation recovery of chalcopyrite and galena under different oxidant oxidation pretreatment systems (flotation conditions: PMS = 1.25 g/L, oxidation time = 15 min, SBX = 2×10^{-4} mol/L). As seen, when using PMS as an oxidant, the recoveries of chalcopyrite and galena decrease as the increase of pH value. When the pH value reaches 8, the recovery of galena is near zero, implying the alkaline pulp environment is beneficial to the depression of galena. For $NaClO$ and H_2O_2 , the variation of recovery as pH value presents a similar tendency.

Fig. 3 displays the oxidant dosage of on flotation recovery of chalcopyrite and galena under different oxidation pretreatment systems (flotation conditions: Oxidation time = 15 min, SBX = 2×10^{-4} mol/L, pH = 8). It can be seen that, for chalcopyrite, the recovery was barely changed as the increase of PMS dosage at the initial stage and sharply decreased when the PMS dosage exceeds to 0.375 g/L. While for galena, the recovery was significantly decreased with the increase in PMS dosage. When the PMS dosage reaches 0.5 g/L, the recovery decreased to 1.50%, indicating the complete depression of galena at this PMS dosage. The optimum PMS dosage for flotation separation of galena and chalcopyrite should be 0.375 g/L. Moreover, as presented in Fig. 3, the depression ability of $NaClO$ on galena is much lower than that of PMS. Although H_2O_2 has excellent depression ability on galena, the chalcopyrite would be also strongly depressed in the same condition. All in all, the above results indicate that the PMS has a much better oxidation effect or selectivity than that of H_2O_2 and $NaClO$ for use as oxidants.

Fig. 4 shows the effect of butyl xanthate dosage on the flotation behavior of chalcopyrite and galena (pH = 8, oxidant = 0.375 g/L, oxidation time = 15 min) with PMS oxidant. It can be seen that the flotation recovery of chalcopyrite significantly increased with the increase of SBX dosage and barely changed when SBX dosage reaches 2×10^{-4} mol/L. In comparison, for galena, the recovery maintains at a low level all the time when the SBX dosage is below 2×10^{-4} mol/L and sharply increased as the SBX dosage is excess 2×10^{-4} mol/L. The optimum dosage of SBX for flotation separation of galena and chalcopyrite should be 2×10^{-4} mol/L. At this point, the recovery rate of galena and chalcopyrite is about 16.1% and 83.8%, respectively.

In addition, artificially mixed minerals flotation tests were conducted to further verify the effect of PMS pretreatment on the flotation separation of chalcopyrite and galena. The flotation products were determined using the inductively coupled plasma optical emission spectrometry (ICP-OES) method.

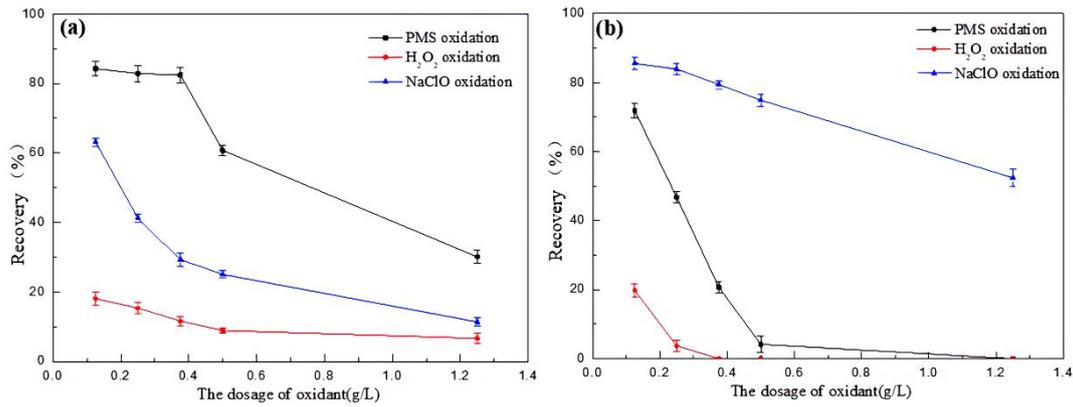


Fig. 3 Effects of oxidant dosage on flotation recovery of chalcopyrite (a) and galena (b) under different oxidation pretreatment systems

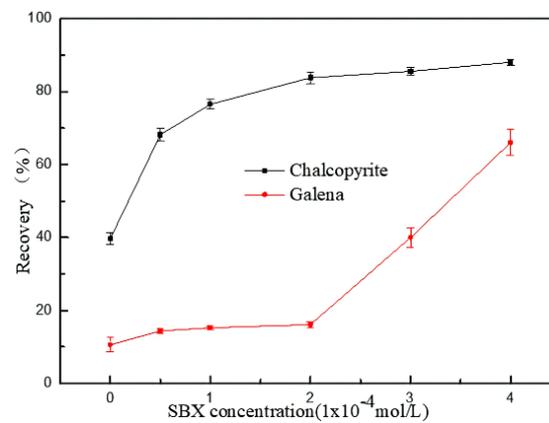


Fig. 4 Effects of collector (SBX) dosage on flotation behavior of chalcopyrite and galena under PMS pretreatment system.

The samples were acidified with hydrochloric acid by high temperature alkali melting method, and the flotation products were continuously measured by ICAP PRO plasma emission spectrometer (Thermo Fisher Instruments).

The test results were shown in Table.2 (flotation conditions: pH=8, SBX=2×10⁻⁴ mol/L). The results show that almost all of the galena entered into the concentrates with an oxidant, which proves that the separation between the two is tough without any oxidants. When using PMS oxidation, it can obtain a high-quality concentration with Cu recovery of 83.66% percentage points and Pb recovery of only 36.10%, which confirms the separation effect is better than the separation effect when using nothing oxidant. The results of mixed ore flotation are consistent with those of single mineral flotation, which proves the feasibility of separating chalcopyrite and galena by oxidation with PMS.

Table. 2 Results of flotation separation of chalcopyrite and galena mixed minerals

Oxidant	Product	Yield (%)	Pb grade (%)	Cu grade (%)	Pb recovery (%)	Cu recovery (%)
Without	Concentrates	95.27	43.52	15.03	92.38	91.97
	Tailings	4.73	7.23	2.64	7.62	8.03
	Feed	100	44.88	15.57	100	100
PMS (0.375 g/L)	Concentrates	60.50	26.78	21.53	36.10	83.66
	Tailings	39.50	72.60	6.44	63.90	16.34
	Feed	100	44.88	15.57	100	100

3.2. Contact angle test analysis

The flotation performance of a mineral can be inferred from its surface hydrophobicity, typically assessed by quantifying the contact angle formed by droplets on the mineral surface. The contact angles of chalcopyrite and galena were measured under various experimental conditions, as depicted in Fig.5a and Fig.5b. The contact angles of untreated chalcopyrite and galena are 88.38° and 79.59°, respectively, indicating their favorable inherent floatability (Huang et al., 2014).

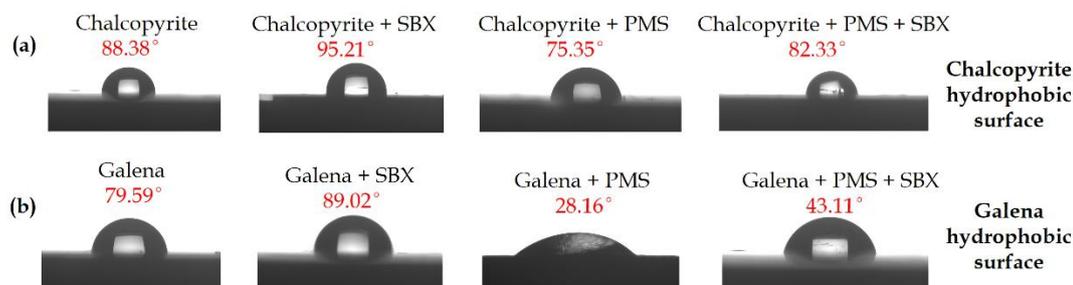


Fig. 5. Contact angles of chalcopyrite (a) and galena (b) before and after reaction with different agents

After treatment with 2×10^{-4} mol/L SBX, the contact Angle of chalcopyrite and galena increased to 95.57° and 89.11° respectively, and the hydrophobicity of the two minerals was significantly enhanced, indicating that SBX could capture the two minerals without selectivity. The contact Angle of chalcopyrite and galena decreased by 13.03° and 51.43° respectively when the PMS dose was 0.375 g/L. Successive PMS and SBX treatments resulted in an increase in galena contact Angle from 22.16° to 43.11° and chalcopyrite contact Angle from 75.35° to 82.33°. This observation suggests that the presence of PMS has minimal impact on the surface hydrophobicity of chalcopyrite, thereby facilitating effective adsorption of the collector. In contrast, galena's hydrophobicity experiences a significant decrease upon interaction with PMS, indicating strong inhibition caused by PMS oxidation, which is consistent with the flotation outcomes.

3.3. Ion concentration analysis

After oxidizing chalcopyrite and galena with different amounts of PMS (the dosage condition of PMS is set the same as that of the micro-flotation test), the oxidized filtrate is collected and chemical analysis of Pb ion concentration and Cu ion concentration is carried out. The test results are shown in Fig. 6.

It can be seen that with the increase in the dosage of PMS, the concentration of Cu ions in the filtrate after chalcopyrite oxidation is almost unchanged, and the concentration remains unchanged when the dosage of PMS is greater than 0.375 g/L. However, the concentration of Pb ion in the filtrate after galena oxidation decreased significantly, and the concentration remained unchanged when the dosage of PMS was greater than 0.5 g/L. It follows that after oxidation of PMS, lead ions dissolved from galena are significantly lower than copper ions dissolved from chalcopyrite. It may be that the oxidized layer formed on the surface of the galena is difficult to dissolve, which makes the hydrophilicity of the galena increase. Although chalcopyrite is also oxidized on its surface, the oxidized layer dissolved in water and fell off, so it maintained good floatability.

Combined with the micro-flotation test results, this proves that the oxidation of PMS has little effect on chalcopyrite, and there are still Cu species dissolved into the solution during the oxidation process. However, its oxidation effect on galena is obvious, and an oxidation film will be formed on the surface of galena, thus preventing the dissolution of Pb ions, and selectively increasing the difference between chalcopyrite and galena in floatability.

3.4. XPS analysis

XPS can effectively detect the element composition, content, and chemical state of mineral surface (Liu et al., 2015). Therefore, XPS detection was further conducted to study the changes in surface chemical states of galena and chalcopyrite before and after PMS oxidation, to characterize the surface species of PMS adsorbed on minerals. XPS analysis was performed with an X-ray photoelectron spectrometer

using an Al K α sputtering ray source operated at 12.0 kV and 6.0 mA. The pressure in the analytical chamber was 1.0×10^{-8} Pa. All binding energies were referenced to the standard C-C binding energy at 284.80 eV to compensate for the surface-charging effects, and XPS software Thermo Advantage 5.976 was utilized to fit and analyze the XPS peaks. The results are shown in Fig. 7 and Fig. 8.

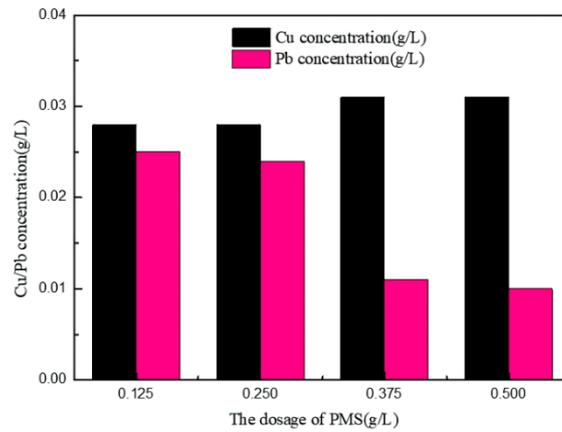


Fig. 6. The concentration of copper (Cu) and lead (Pb) at pH=8 under different dosages of PMS

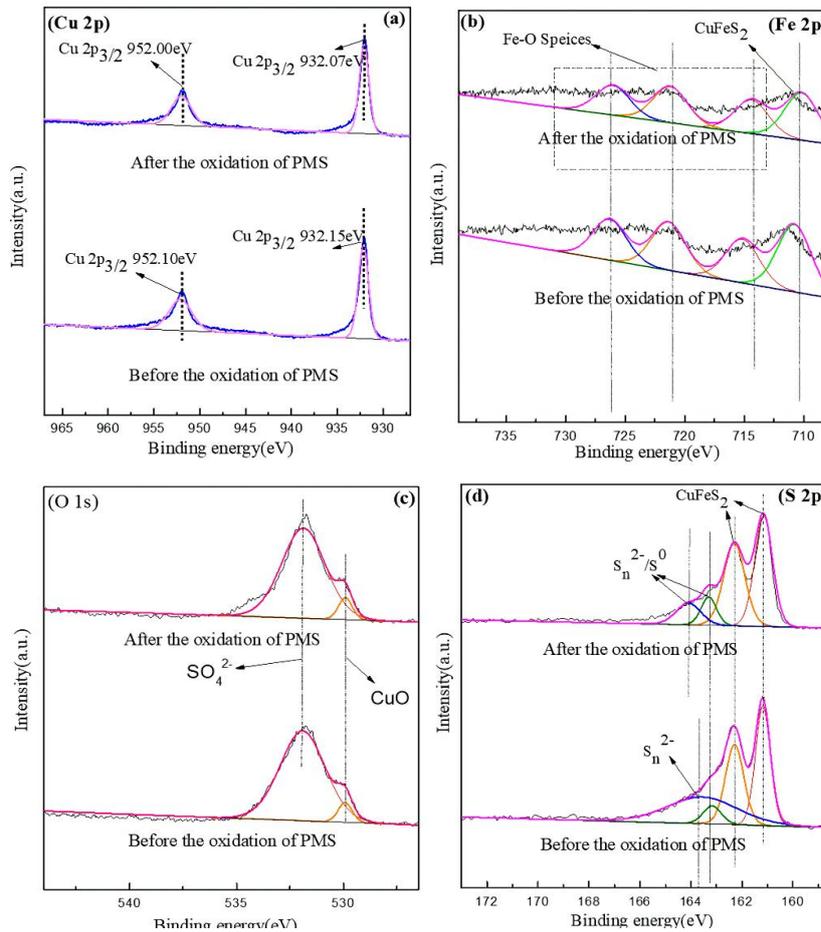


Fig. 7. The High-resolution XPS spectra of the chalcopyrite before and after XPS oxidation pretreatment: (a) Cu 2p; (b) Fe 2p; (c) O 1s; (d) S 2p.

The high-resolution spectra of Cu 2p, Fe 2p, O 1s, and S 2p of chalcopyrite before and after PMS oxidation are shown in Fig. 7. Fig. 7a describes the high-resolution spectra of chalcopyrite Cu 2p before and after oxidation. It can be seen that the two peaks with the binding energy centers of 932.07 eV and

952.00 eV correspond to Cu 2p_{3/2} and Cu 2p_{1/2} in the original chalcopyrite (Hirajima. T et al., 2017; Hirajima. T et al., 2014). Fig. 7b describes the high-resolution spectra of Fe 2p of chalcopyrite before and after oxidation. For the original chalcopyrite, the peaks at the binding energy of 710.78 eV correspond to CuFeS₂, and the peaks at the binding energy of 715.14 eV, 721.35 eV and 726.30 eV indicate iron oxides (FeOOH, FeSO₄) (T. Hirajima et al., 2017; G.R. da Silva et al., 2018), which can be attributed to slight oxidation during the preparation of chalcopyrite samples by crushing and grinding. For the oxidized chalcopyrite, slight changes in the positions and proportions of all peaks indicate a slight increase in surface oxidation. Fig. 7c describes the high-resolution spectra of chalcopyrite at O 1s before and after oxidation. The peaks at the binding energy of 529.92 eV and 531.91 eV on the surface of the original chalcopyrite represent CuO and sulfate species (Hirajima. T et al., 2017; Suyantara. GPW et al., 2018a; Hirajima. T et al., 2014), respectively, which are also attributed to slight oxidation in the air during sample preparation. Fig. 7d describes the high-resolution spectra of chalcopyrite S 2p before and after oxidation. It can be seen that the peaks located at the binding energy of 160 eV~165 eV indicate the surface of untreated chalcopyrite is composed of CuFeS₂ species (161.18 eV and 162.29 eV), sulfur (S⁰, 163.17 eV) and polysulfide (S_n²⁻, 163.56 eV) species (da Silva. GR et al., 2018; Ozun. S et al., 2019; Velásquez. P et al., 1998), respectively. In contrast, as present in Fig.7, after oxidation treatment, little changes can be observed in the spectra of Cu 2p, Fe 2p, O 1s, and S 2p.

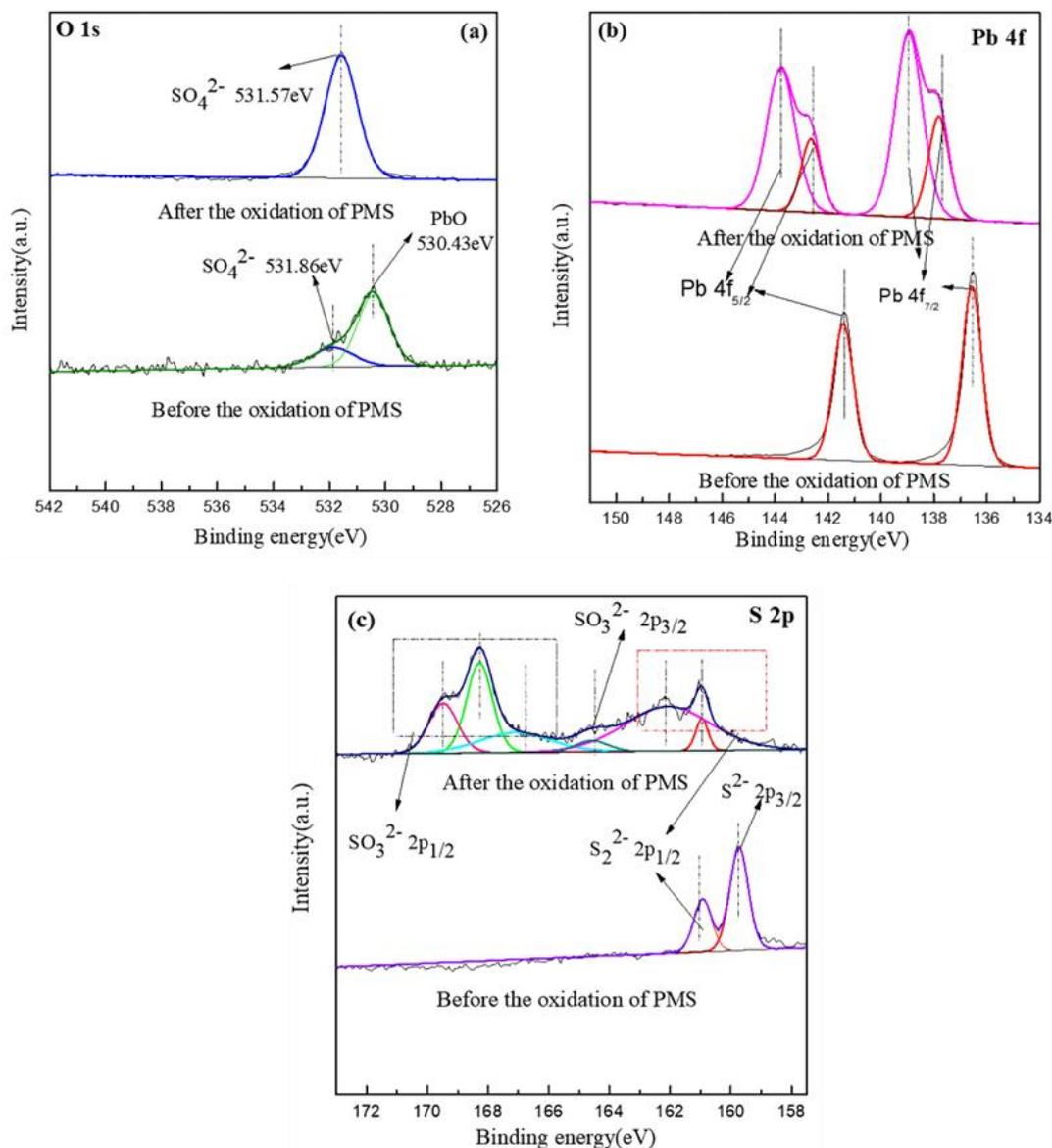


Fig. 8. The High-resolution XPS spectra of the galena before and after XPS oxidation pretreatment: (a) O 1s; (b) Pb 4f; (c) S 2p

Fig 8 displays the high-resolution spectra of O 1s, Pb 4f, and S 2p of galena before and after PMS oxidation. Fig. 8a describes the high-resolution spectra of galena O 1s before and after oxidation. It can be seen that for the original galena, the peak at the binding energy of 530.43eV and 531.86eV can be attributed to PbO and SO_4^{2-} (Wang et al., 2021; Su et al., 2022b), which may be due to slight oxidation of the sample during the preparation process. After being oxidized by PMS, only the peak at the binding energy of 531.57 eV can be detected, which represents the species of SO_4^{2-} . The oxidation product on the surface of the galena should be PbSO_4 (Yang et al., 2022).

The high-resolution spectra of galena Pb 4f before and after oxidation are shown in Fig. 8b. The spectra of the original galena consist of a set of bi-peaks with binding energies of 136.56 eV and 141.43 eV respectively, which can be attributed to PbS. After being oxidized by PMS, a new separation peak appeared at 138.95 eV and 143.78 eV, which can be attributed to PbSO_4 species (Xie et al., 2021; Huang et al., 2019). The two peaks binding energy at 136.56 eV and 141.43 eV was shifted to 137.82 eV and 142.65 eV, respectively. the strength of the two peaks was also significantly decreased. The results confirm the surface of galena was sharply oxidized by PMS in the oxidation pretreatment process and the oxidation product should be PbSO_4 .

Fig. 8c shows the high-resolution spectra of galena S 2p before and after oxidation. The peaks at 159.73 eV, 160.93 eV, and binding energy in the figure are attributed to $\text{S}^{2-} 2p_{3/2}$ and $\text{S}_2^{2-} 2p_{1/2}$ on the surface of the original galena. After oxidation, the intensity of $\text{S}_2^{2-} 2p_{1/2}$ peaks on the galena surface decreased obviously, and many new separation peaks appeared, located at the binding energy of 164.58 eV, 167.12 eV, 168.28 eV, 169.48 eV, which could be allocated to sulfate species (SO_4^{2-} , SO_3^{2-}). It further confirms the generation of PbSO_4 on the galena surface in the oxidation process (Chen et al., 2021).

In general, XPS analysis results show that the surface properties of galena were greatly changed in the oxidation process. The amount of PbSO_4 oxidation product was generated and covered on the surface of the galena. For chalcopyrite, in relative terms, the surface is little affected in the oxidation process.

3.5. ESR analysis

In the catalytic area, it is known that metallic oxide or metal oxide or sulfide can be used as a catalyst for PMS to generation of free radicals. The free radical has a much strong oxidation ability than that of the oxidant itself. To better understand the oxidation mechanism of the PMS on galena and chalcopyrite, ESR measurement by using DMPO as a spin-trapping agent was carried out to confirm the existence of hydroxyl radical ($\cdot\text{OH}$) and sulfate radical ($\text{SO}_4^{\cdot-}$), and the result is presented in Fig. 9.

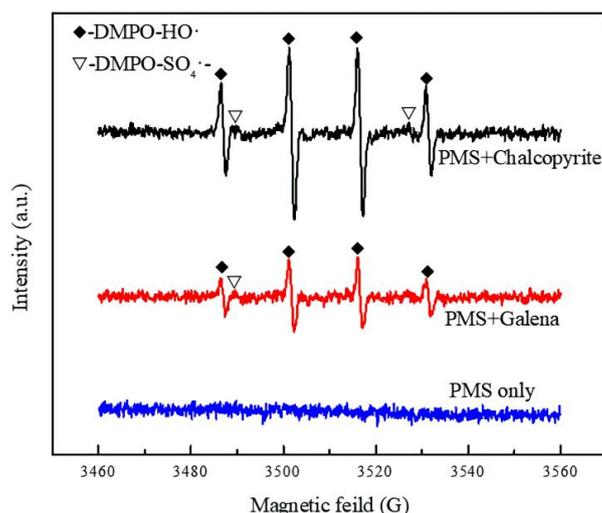


Fig. 9. ESR spectra of DMPO spin-trapping adducts in different systems

As seen, no signals were detected when PMS alone exists in the solution, indicating no radicals were generated under the condition. While, for both chalcopyrite and galena, clearly, the ESR curves show that 4-fold characteristic peaks with an intensity ratio of 1:2:2:1. This implies the $\cdot\text{OH}$ was generated in the chalcopyrite and galena pretreatment process. Moreover, as marked in Fig. 9, the characteristic

signals of $\text{SO}_{\text{also}}^{\cdot-4}$ can be found in the ESR curves. Obviously, the $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ were generated in the pretreatment process, which possibly enhance the oxidation effect. In addition, the intensity of ESR spectra of chalcopyrite is much higher than that of galena. This indicates that more radicals generate in the chalcopyrite oxidation pretreatment process.

3.6. AFM analysis

The influence of PMS treatment on the surface of chalcopyrite and galena before and after PMS treatment was further examined by AFM, and the result is shown in Fig. 10.

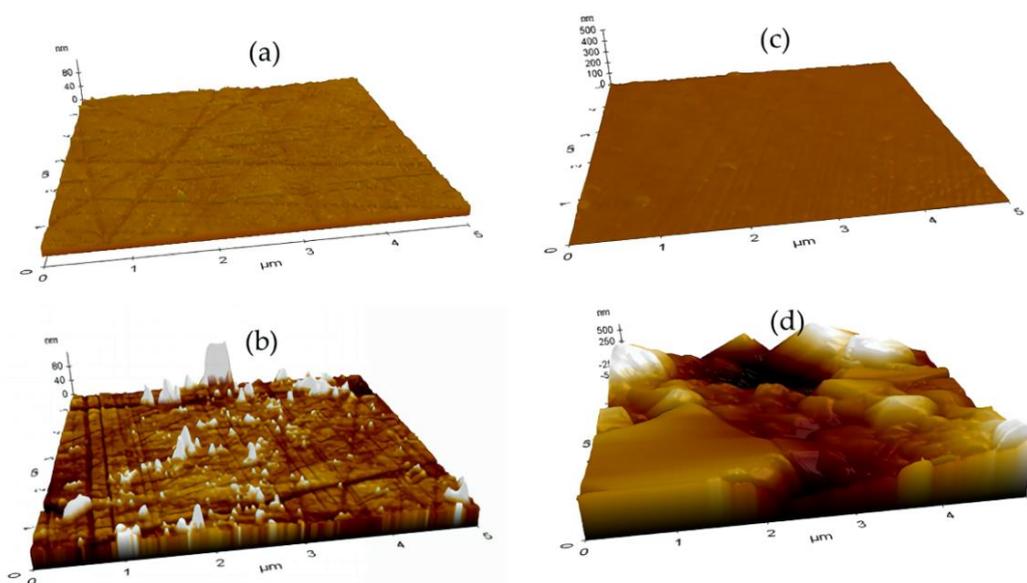


Fig. 10. AFM images of different samples: (a) Pristine chalcopyrite; (b) Oxidation pretreated chalcopyrite; (c) Pristine galena; (d) Oxidation pretreated galena

It can be seen from Fig. 10a and Fig. 10c, pristine chalcopyrite and galena has flat and uniform surface. In contrast, as presented in Fig. 10b, some mountainous features appeared on the surface of chalcopyrite after being oxidized by PMS. While, for galena, almost all of the surface was covered by mountainous features. This difference indicates the oxidation degree of galena is much higher than that of chalcopyrite.

Table 3. Surface roughness of chalcopyrite and galena before and after oxidation.

Product	Before oxidation		After oxidation	
	Rq(nm)	Ra(nm)	Rq(nm)	Ra(nm)
chalcopyrite	2.756	2.067	6.109	3.336
galena	3.409	2.455	199.000	149.000

Based on AFM measurement, Table 3 presents the surface roughness of chalcopyrite and galena before and after PMS treatment. For chalcopyrite, the Ra increased from 2.076 nm to 3.336 nm after PMS oxidation. While, for galena, it increased from 2.455 nm to 149.000nm. This further confirms that the oxidation degree of galena is much higher than that of chalcopyrite.

3.7. Possible mechanisms

Combined with the flotation results, XPS, ESR, and AFM results, a schematic model is proposed in Fig.11 to illustrate the effect of oxidation on the flotation separation process of chalcopyrite and galena. In the oxidation process, for galena, the surface was severely oxidized due to the strong oxidizing

property and the generation of free radical radicals ($\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$). The XPS measurement results indicate the oxidation product is PbSO_4 . The PbSO_4 is derived from the oxidation of PbS on the surface of galena. Thus, there is a significant opportunity for PbSO_4 to cover the surface of the galena and form an oxidation layer subsequent to PMS oxidation. This resulting oxidation layer effectively hinders contact between the collector and the surface, thereby depressing galena flotation even in the absence of a depressant. In comparison, the oxidation extent of chalcopyrite is much lower than that of galena, which still maintains excellent floatability. The possible reason is that the oxidation product of chalcopyrite is CuSO_4 , which can be dissolved in solution (as analyzed in Chapter 3.2). On the whole, the oxidation pretreatment by PMS caused great disparities in the surface properties of chalcopyrite and galena, resulting in the flotation separation of the two minerals.

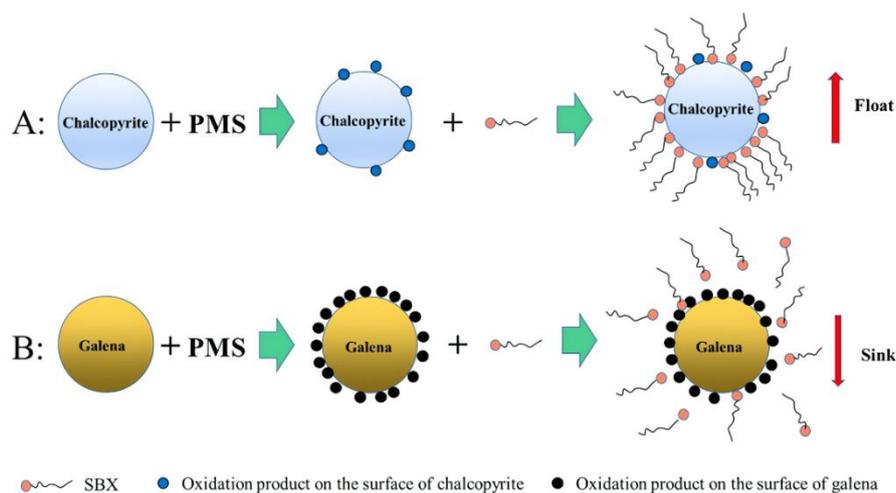


Fig. 11. The conceivable mechanism of surface oxidation using PMS as oxidant on separation of chalcopyrite and galena

4. Conclusions

In this study, it is found that the pre-oxidation method using PMS as an oxidant is an effective way to separate chalcopyrite and galena. The flotation results indicate that at $\text{pH}=8$, with a raw ore containing 44.88% Pb and 15.57% Cu, adding 0.375 g/L of PMS can yield a flotation concentrate with a Pb grade of 26.78% and recovery rate of 36.10%, as well as a Cu grade of 21.53% and recovery rate of 83.66%. After PMS oxidation pretreatment, galena lost its natural floatability and even could not be recovered by the addition of an SBX collector. In comparison, chalcopyrite still kept good floatability. Based on this method, the flotation separation of Cu-Pb was effectively achieved. Mechanism analysis shows that the application of PMS can oxidize galena well so that more hydrophilic oxides are generated on the surface of galena, which inhibits galena flotation. At the same time, the oxidation of PMS has little effect on chalcopyrite, so PMS shows excellent oxidation and selectivity in the separation of the two. All in all, the above results indicate that PMS pre-oxidation is a high-potential method in practical chalcopyrite galena flotation separation, and PMS can be used as a new agent with high efficiency and environmental protection to replace traditional oxidants.

Acknowledgments

This work was supported by the National key research and development program (grant no. 2018YFC19016); The Youth Jinggang Scholars Program in Jiangxi Province (grant no. QNJG2020048); The Program of Qingjiang Excellent Young Talents, Jiangxi University of Science and Technology (grant no. JXUSTQJBJ2020002).

References

CAO, M., LIU, Q., 2006. *Reexamining the functions of zinc sulfate as a selective depressant in differential sulfide flotation – the role of coagulation*. J. Colloid Interface Sci. 301(2), 523–531.

- CHEN, Y., FENG, B., GUO, Y., WANG, T., ZHANG, Y., ZHONG, C., WANG, H., 2021. *The role of oxidizer in the flotation separation of chalcopyrite and galena using sodium lignosulfonate as a depressant*. Miner. Eng. 172, 107160.
- DA, S., WATERS, K., 2018. *The effects of microwave irradiation on the floatability of chalcopyrite, pentlandite and pyrrhotite*. Adv. Powder Technol. 29, 3049–3061.
- HIRAJIMA, T., MIKI, H., SUYANTARA, G., MATSUOKA, H., ELMAHDY, A., SASAKI, K., IMAIZUMI, Y., KUROIWA, S., 2017. *Selective flotation of chalcopyrite and molybdenite with H₂O₂ oxidation*. Miner. Eng. 100, 83–92.
- HIRAJIMA, T., MORI, M., ICHIKAWA, O., SASAKI, K., MIKI, H., FARAHAT, M., SAWADA, M., 2014. *Selective flotation of chalcopyrite and molybdenite with plasma pre-treatment*. Miner. Eng. 66, 102–111.
- HUANG, P., CAO, M., LIU, Q., 2012. *Using chitosan as a selective depressant in the differential flotation of Cu–Pb sulfides*. Int. J. Miner. Process. 106, 8–15.
- HUANG, P., WANG, L., LIU, Q., 2014. *Depressant function of high molecular weight polyacrylamide in the xanthate flotation of chalcopyrite and galena*. Int. J. Miner. Process. 128, 6–15.
- HUANG, X., JIA, Y., CAO, A., WANG, S., MA, X., ZHONG, H., 2019. *Investigation of the interfacial adsorption mechanisms of 2-hydroxyethyl dibutyl dithiocarbamate surfactant on galena and sphalerite*. Colloids Surf. A Physicochem. Eng. Asp. 583, 123908.
- LEI, H., JIANG, T., GUO, X., TIAN, Q., ZHONG, S., DONG, L., QIN, H., LIU, Z., BRIAN, M., 2023. *Sustainable processing of gold cyanide tailings: Reduction roasting, mechanical activation, non-cyanide leaching, and magnetic separation*. Hydrometallurgy. 217, 106028.
- LIU, G., QIU, Z., WANG, J., LIU, Q., XIAO, J., ZENG, H., ZHONG, H., XU, Z., 2015. *Study of N-isopropoxypropyl-N'-ethoxycarbonyl thiourea adsorption on chalcopyrite using in situ SECM, ToF-SIMS and XPS*. J. Colloid Interface Sci. 437, 42–49.
- LIU, Q., LASKOWSKI, J., 1989. *The role of metal hydroxides at mineral surfaces in dextrin adsorption, II. Chalcopyrite-galena separations in the presence of dextrin*. Int. J. Miner. Process. 27(1–2), 147–155.
- LIU, Q., ZHANG, Y., 2000. *Effect of calcium ions and citric acid on the flotation separation of chalcopyrite from galena using dextrin*. Miner. Eng. 13(13): 1405–1416.
- MIAO, Y., WEN, S., SHEN, Z., FENG, Q., ZHANG, Q., 2022. *Flotation separation of chalcopyrite from galena using locust bean gum as a selective and eco-friendly depressant*. Sep. Purif. Technol. 283, 120173.
- MU, Y., PENG, Y., LAUTEN, R., 2016. *The depression of pyrite in selective flotation by different reagent systems—A Literature review*. Miner. Eng. 96, 143–156.
- OZUN, S., HASSAS, B., MILLER, J., 2019. *Collectorless flotation of oxidized pyrite*. Colloids Surf. A. 561, 349–356.
- RATH, R., SUBRAMANIAN, S., PRADEEP, T., 2000. *Surface chemical studies on pyrite in the presence of polysaccharide-based flotation depressants*. J. Colloid Interface Sci. 229(1), 82–91.
- SU, C., CAI, J., YU, X., PENG, R., ZHENG, Q., MA, Y., LIU, R., SHEN, P., LIU, D., 2022a. *Effect of pre-oxidation on galena in the flotation separation of chalcopyrite from galena with calcium lignosulfonate as depressant*. Miner. Eng. 182, 107520.
- SU, C., CAI, J., YU, X., PENG, R., ZHENG, Q., MA, Y., LIU, R., SHEN, P., LIU, D., 2022b. *Effect of pre-oxidation on galena in the flotation separation of chalcopyrite from galena with calcium lignosulfonate as depressant*. Miner. Eng. 182, 107520.
- SUYANTARA, G., HIRAJIMA, T., MIKI, H., SASAKI, K., YAMANE, M., TAKIDA, E., KUROIWA, S., IMAIZUMI, Y., 2018a. *Selective flotation of chalcopyrite and molybdenite using H₂O₂ oxidation method with the addition of ferrous sulfate*. Miner. Eng. 122, 312–326.
- SUYANTARA, G., HIRAJIMA, T., MIKI, H., SASAKI, K., YAMANE, M., TAKIDA, E., KUROIWA, S., IMAIZUMI, Y., 2018b. *Effect of Fenton-like oxidation reagent on hydrophobicity and floatability of chalcopyrite and molybdenite*. Colloids Surf. A. 554, 34–48.
- TANG, X., CHEN, Y., LIU, K., ZENG, G., PENG, Q., LI, Z., 2019. *Selective flotation separation of molybdenite and chalcopyrite by thermal pretreatment under air atmosphere*. Colloids Surf. A Physicochem. Eng. Asp. 583, 123958.
- TANG, X., HUANG, X., LIU, K., FENG, Q., LIU, Z., AO, M., 2018. *Synthesis of magnetically separable MnO₂/Fe₃O₄/Silica nanofiber composite with enhanced Fenton-like catalytic activity for degradation of Acid Red 73*. Surface&Coatings Technol. 354, 18–27.
- VELASQUEZ, P., GOMEZ, H., RAMOS-BARRADO, J., LEINEN, D., 1998. *Voltammetry and XPS analysis of a chalcopyrite CuFeS₂ electrode*. Colloids Surf. A. 140, 369–375.
- WANG, C., LIU, R., SUN, W., JING, N., XIE, F., ZHAI, Q., HE, D., 2021. *Selective depressive effect of pectin on sphalerite flotation and its mechanisms of adsorption onto galena and sphalerite surfaces*. Miner. Eng. 170, 106989.

- WEI, G., FENG, B., PENG, J., ZHANG, W., ZHANG, X., 2019. *Depressant behavior of tragacanth gum and its role in the flotation separation of chalcopyrite from talc*. J. Mater. Res. Technol. 8(1), 697–702.
- XIE, H., LIU, Y., RAO, B., WU, J., GAO, L., CHEN, L., TIAN, X., 2021. *Selective passivation behavior of galena surface by sulfuric acid and a novel flotation separation method for copper-lead sulfide ore without collector and inhibitor*. Sep. Purif. Technol. 267, 118621.
- YANG, S., TANG, X., CHEN, R., FAN, X., MIAO, J., LUO, X., 2023. *Application of maleic acid-acrylic acid copolymer as an eco-friendly depressant for effective flotation separation of chalcopyrite and galena*. Minerals, 13(2), 191.
- YANG, S., XU, Y., LIU, C., AI, G., HUANG, L., YU, H., 2020. *A novel method to achieve the flotation of pyrite from lizardite slime without collector or depressant*. Miner. Eng. 157, 106580.
- YANG, X., HUANG, X., QIU, T., 2016. *Activation-flotation kinetics of depressed marmatite and chalcopyrite in cyanidation tailings using sodium hypochlorite as activator*. Miner. Metall. Process. 33, 131–136.
- YANG, Z., GENG, L., ZHOU, H., LIU, Z., XIE, F., YANG, S., LUO, X., 2022. *Improving the flotation separation of chalcopyrite from galena through high-temperature air oxidation pretreatment*. Miner. Eng. 176, 107350.
- YI, G., MACHA, E., VAN, D., MACHA, R., MCKAY, T., FREE, M., 2021. *Recent progress on research of molybdenite flotation: a review*. Adv. Colloid Interface Sci. 295, 102466.
- ZHANG, J., ZHANG, X., WEI, X., CHENG, S., HU, X., LUO, Y., XU, P., 2022b. *Selective depression of galena by sodium polyaspartate in chalcopyrite flotation*. Miner. Eng. 180, 107464.
- ZHANG, L., GUO, X., TIAN, Q., LI, D., ZHONG, S., QIN, H., 2022a. *Improved thiourea leaching of gold with additives from calcine by mechanical activation and its mechanism*. Miner. Eng. 178, 107403.
- ZHANG, X., ZHU, Y., ZHENG, G., HAN, L., MCFADZEAN, B., QIAN, Z., PIAO, Y., O'CONNOR, C., 2019. *An investigation into the selective separation and adsorption mechanism of a macromolecular depressant in the galena-chalcopyrite system*. Miner. Eng. 134, 291–299.
- ZHANG, Z., WANG, Y., LIU, G., LIU, S., LIU, J., YANG, X., 2020. *Separation of chalcopyrite from galena with 3-amyl-4-amino-1,2,4-triazole-5-thione collector: Flotation behavior and mechanism*. J. Ind. Eng. Chem. 92, 210–217.
- ZHU, H., YANG, B., MARTIN, R., ZHANG, H., HE, D., LUO, H., 2022. *Flotation separation of galena from sphalerite using hyaluronic acid (HA) as an environmental-friendly sphalerite depressant*. Miner. Eng. 187, 107771.