Effect of preoxidation on copper flotation from copper-lead mixed concentrate

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Abstract: Flotation separation of galena and chalcopyrite is always a difficult problem in mineral processing. In this paper, the selective preoxidation of galena and chalcopyrite with sulfuric acid was developed, and then the two minerals were completely separated by flotation. The surface oxidation mechanism of galena and chalcopyrite with sulfuric acid was analyzed by Fourier transform infrared spectroscopy (FT-IR) and Atomic Force Microscopy (AFM), and the results showed that hydrophilic oxide film was formed on the galena surface, while the surface of chalcopyrite is still hydrophobic sulfide film, which led to the separation of the two minerals by flotation. In addition, the Response Surface Methodology (RSM) was used to analyze the influence of main preoxidation parameters on the flotation separation of copper-lead concentrate, and the parameters were further optimized, as follows: sulfuric acid concentration of 5.3 mol/L, oxidation temperature of 101.8 °C and time of 48.3 min. The mixed concentrate containing Cu 11.57% and Pb 16.75% was preoxidized under the above conditions, and the flotation separation verification results showed that Cu concentrate with Cu grade of 18.09% and recovery of 95.41%, and Pb concentrate with Pb grade of 44.96% and recovery of 95.94% was obtained respectively. This paper provides a new method of preoxidation combined flotation to achieve high-efficiency separation of copper-lead mixed concentrate.

1. Introduction

Copper and lead are common and important non-ferrous metals, which are widely used in military, materials, machinery, metallurgy and other fields (Duang, Yang and Jiang. 2022; Bai et al. 2021). Copper-lead polymetallic sulfide is an important source of copper and lead metal (Fen et al. 2021; Lai et al. 2020). Galena and chalcopyrite are the sources of lead minerals and copper minerals in copper-lead polymetallic sulfide ores respectively. Flotation, as one of the most commonly used and effective methods of mineral processing, has the advantages of environmental protection, efficiency and low cost, and is the most commonly used method for recovering copper and lead minerals from copper-lead polymetallic sulfides (Ke and Chen. 2022; Nagaraj and Farinato. 2016; Ma et al. 2016). However, galena and chalcopyrite are very difficult to be separated by flotation because of their good natural floatability (Wang et al. 2021; Liang et al. 2021). Therefore, the separation of copper and lead in industrial production has always been the focus and difficulty of the separation of copper-lead polymetallic sulfide.

At present, mixed flotation process is used to produce mixed concentrate and then galena and chalcopyrite separation is a common method in the flotation of copper-lead polymetallic sulfide (Subramanian, Santhiya and Natarajan. 2003; Sun et al. 2022). Mixed flotation has the advantages of simple reagents, strong adaptability, low energy consumption, and high metal recovery. Copper and lead mixed flotation refers to the simultaneous floating of copper sulfide and lead sulfide minerals to obtain copper-lead mixed concentrate, and finally to produce copper and lead concentrate through further flotation separation (Chen et al. 2016; Zhang et al. 2022; Wang et al. 2019). It is relatively easy to

obtain copper-lead mixed concentrate by flotation, but it is challenging to achieve efficient separation of copper-lead mixed concentrate by flotation. The main reasons for the difficulty of flotation separation of copper-lead mixed concentrate are as follows: (1) chalcopyrite and galena have good and similar floatability (Xie et al. 2019); (2) the intercalation relationship between copper-lead polymetallic sulfide minerals is relatively complex, and the wrapping phenomenon is widespread, resulting in incomplete dissociation of the target minerals (Su et al. 2020; Srdjan. 2007); (3) the minerals are oxidized and hydrated in water, resulting in the weakening and destruction of the internal bonds of the mineral lattice, and the interference of dissolved surface ions and the inherent ions in water on flotation (October. 2020; Zhang et al. 2019); (4) the inhibition effect of existing conventional inhibitors is weak, and it is difficult to expand the floatability difference between chalcopyrite and galena (Patra and Natarajan. 2008; Liu et al. 2013). Therefore, it is of great significance to achieve efficient flotation separation of copper-lead polymetallic sulfides.

In this paper, galena-chalcopyrite artificial mixed ore and copper-lead mixed concentrate from Yunnan Province of China were studied, and good results of copper and lead separation were obtained by sulfuric acid preoxidation-flotation separation process. Firstly, the surface reaction mechanism of galena and chalcopyrite with sulfuric acid was characterized and analyzed by Fourier transform infrared spectroscopy (FT-IR) and Atomic Force Microscopy (AFM). The results showed that sulfuric acid was used as a preoxidation agent to selectively generate PbSO4 oxide film on galena surface, which greatly reduced the floatability of galena. Chalcopyrite still maintains excellent floatability, so that the two minerals can be effectively separated. In addition, the Response Surface Methodology (RSM) was used to optimize sulfuric acid preoxidation parameters and guide the separation of copper and lead from actual mixed concentrates. RSM is a method to optimize test parameters by combining separation data with experimental designer method using statistics and mathematics. Finally, the flotation separation test of copper-lead sulfide mixed concentrate was carried out by using the optimized preoxidation parameters of RSM, and a good separation index of copper and lead was achieved. The feasibility of sulfuric acid preoxidation and flotation separation process is demonstrated in this study, which provides a research basis for the efficient separation of copper-lead polymetallic sulfide.

2.   Materials and experiment

2.1.   Materials and reagents

2.1.1. Galena and chalcopyrite single mineral samples

The galena and chalcopyrite used in the test were taken from Dali City, Yunnan Province, China. High-grade single minerals were obtained through manual purification, grinding, screening, and re-separation. The results of multi-element analysis were respectively shown in Table 1 and Table 2. As can be seen from Table 1 and Table 2, the Pb content of the galena single mineral is 84.42%, and the purity is 96.64%. The content of Cu in chalcopyrite single mineral is 33.15%, and the purity is 95.15%, both of which contain a small amount of impurities to meet the test requirements.

Table 1. Chemical multi-element analysis results of galena single mineral

Component	Pb	S	Zn	SiO$_2$	Other impurities
Content/%	84.42	9.15	0.13	3.95	2.35

Table 2. Chemical multi-element analysis results of chalcopyrite single mineral

Component	Cu	S	Fe	SiO$_2$	Other impurities
Content/%	33.15	33.16	28.98	2.39	2.32

2.1.2. Copper-lead mixed concentrate

The copper-lead sulfide mixed concentrate used in the test was taken from Dali City, Yunnan Province, China. The -400 mesh (-0.038 mm) of the mixed concentrate accounts for 94.41%, which belongs to fine particles and about 80% of the particles are completely dissociated from chalcopyrite and galena, which are continuously related to other minerals or gangues. The main chemical multi-element analysis,

mineral types and contents are shown in Table 3, Table 4 and Fig. 1 respectively. It can be seen from Table 3, the mixed concentrate mainly contains Cu 11.57%, Pb 16.75%, S 27.98%, Cu and Pb are mixed with high content, which requires further separation. Gangue components are mainly small amounts of SiO_2, Al_2O_3, CaO and MgO. As can be seen from Table 4 and Fig. 1 that the main copper mineral in the mixed concentrate is chalcopyrite and lead mineral is galena, in which the content of $CuFeS_2$ is 33.26% and PbS is 19.34%. Gangue minerals are mainly quartz, dolomite and calcite.

Table 3. Results of multi-element analysis of copper-lead sulfide mixed concentrate

Components	Cu	Pb	S	TFe
Content /%	11.57	16.75	27.98	27.63
Components	SiO_2	CaO	Zn	MgO
Content /%	5.32	1.96	1.17	0.89

Table 4. Main mineral composition of copper-lead sulfide mixed concentrate

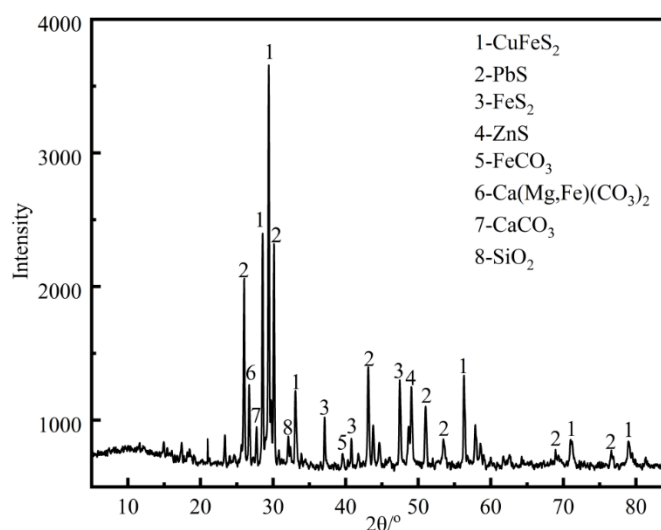| Mineral	Chalcopyrite	Galena	Pyrite	Sphalerite
Molecular formula	$CuFeS_2$	PbS	FeS_2	ZnS
Content /%	33.26	19.34	17.19	3.55
Mineral	Dolomite	Calcite	Quartz	Siderite
Molecular formula	$Ca(Mg,Fe)(CO_3)_2$	$CaCO_3$	SiO_2	$FeCO_3$
Content /%	5.72	4.19	5.35	5.56

Fig. 1. XRD analysis of copper and lead sulfide mixed concentrate

2.1.3. Reagents

The reagents of sulfuric acid (H_2SO_4, 98%, Chengdu Kelong Reagent Factory, China), butylxanus ($C_4H_9OCSSNa$, Chengdu Kelong Reagent Factory, China), and terpineol oil (C10H17OH, Yunnan Tiefeng Pharmaceutical Factory, China) were used as preoxidation agent, collector, and foaming agent respectively. The water used in the experiments was deionized (DI) water .

2.2. Flotation separation test for mixed concentrate

2.2.1. Preoxidation test

Firstly, sulfuric acid preoxidation of galena and chalcopyrite was carried out. A solution of sulfuric acid of a certain concentration is prepared, and 50ml of the solution is placed in a beaker and heated to a

given temperature. The galena and chalcopyrite with a particle size of -0.038mm were cleaned by ultrasonic wave for several times, then weighed 2.0g and put into the beaker, and stirred for a certain time with a magnetic stirrer at the speed of 300 r/min. Then, FT-IR and AFM tests were conducted on the pre-treated minerals after filtration, washing and natural drying.

Secondly, the sulfuric acid preoxidation test of copper and lead mixed concentrate was carried out. The effect of sulfuric acid concentration, preoxidation temperature, and time on the flotation separation of copper-lead mixed concentrate were investigated. In order to reduce the error, each group of tests was repeated 3 times, and the results were averaged. The mixed concentrate of each preoxidation test was 100.0 g, the liquid-solid ratio was 2:1, and the stirring speed was 200 r/min. The sulfuric acid concentrations were 2.0 mol/L, 3.0 mol/L, 4.0 mol/L, 5.0 mol/L and 6.0 mol/L, respectively. The temperature conditions are 20 °C, 40 °C, 60 °C, 80 °C and 100 °C. The preoxidation time was 10 min, 20 min, 30 min, 40 min, 50 min. The mixed concentrate after sulfuric acid preoxidation was filtered, vacuum-dried at room temperature was used as feed material for flotation separation experiments.

2.2.2 Flotation separation test for mixed concentrate

XFD-0.5 small flotation machine (Xiamen Exploration Machinery Factory, China) was used for flotation experiments. A certain amount of pretreated mixed concentrate sample was added to the flotation tank at a stirring speed of 2000 r/min, the dose of terpineol oil was 80 g/t, the stirring time was set at 3 minutes and the foaming time after adding terpineol oil was 3 minutes, and the whole process is collectorless flotation. After the flotation is completed, the foam products obtained from the completion of flotation were filtered, dried at room temperature, weighed and the Cu grade and recovery in Cu concentrate and the Pb grade and recovery in Pb concentrate were calculated. To minimize error, each set of trials was repeated 3 times and the results are averaged. The experimental flowsheet of preoxidation-flotation separation for copper-lead sulfide mixed concentrate is shown in Fig. 2.
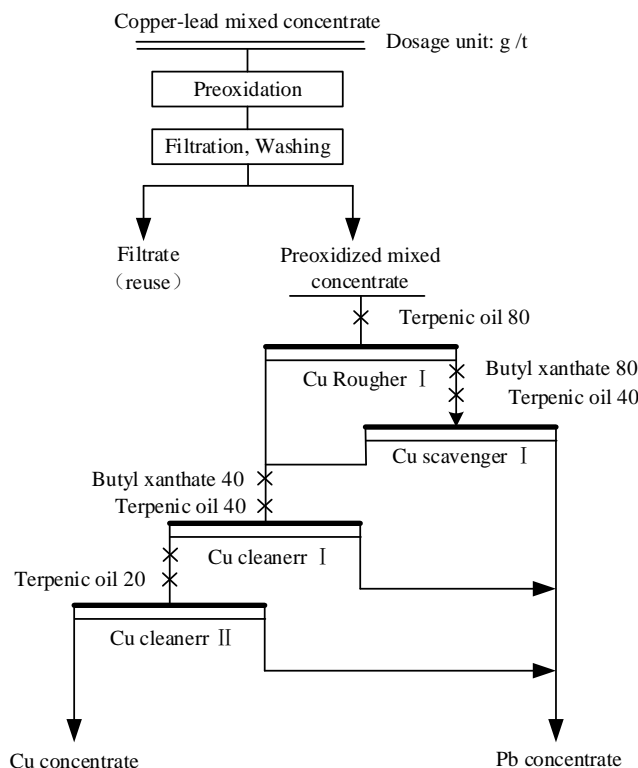

Fig. 2. The flowsheet of preoxidation-flotation for copper-lead mixed concentrate

2.3. FT-IR analysis

Fourier transform infrared spectroscopy (FT-IR) was used to characterize the adsorption of surfactants before and after the interaction between minerals and agents (Chernyshova and Andreev. 1997). The

infrared spectroscopy analysis were performed with the Nicolet Nexus 470 Fourier infrared spectroscopy. The chalcopyrite and galena samples were pretreated with sulfuric acid in a vacuum box at room temperature. After drying, the samples and KBr powder were fully mixed on agate mortar at the ratio of 1 to 50, and then placed on a tablet press to make pellet/tablet pressure for 30 s. After that, the samples were taken out and put into a sample stage for FT-IR analysis.

2.4. AFM analysis

Atomic Force Microscope (AFM) is commonly used for surface structure and properties of minerals through surface morphology study (Leiro, Torhola and Laajalehto. 2017; Somayeh et al. 2020). The surface morphology changes of galena and chalcopyrite before and after sulfuric acid preoxidation were studied by AFM (Bruker Dimension Ico, German). NanoScope software was used to analyze the AFM surface images, and to reveal the surface morphology and surface roughness of galena and chalcopyrite before and after sulfuric acid preoxidation.

2.5. Experimental parameters and optimization method

Response Surface Methodology (RSM) is a statistical test method to optimize the stochastic process, aiming to find the quantitative rule between test index and each influencing factor and the best combination of each factor, and to provide guidance for experiments (Qiu et al. 2018; Rahdar et al. 2021). The key parameters affecting the separation efficiency of galena and chalcopyrite are sulfuric acid concentration, preoxidation temperature and time. Numerical module in the Design-Expert 12 software was used to optimize the analysis. In the experimental design model, Box-Behnken design (BBD) model with three variables, low level and high level, were used to analyze and determine the main influencing factors and level range of copper-lead separation. Variance analysis was performed on the test results to clarify the influence of each factor on the separation of copper-lead mixed concentrate. Multiple regression fitting and regression models were established to optimize the acid preoxidation parameters. It is further used to guide the flotation separation of the mixed concentrate.

3.   Results and discussion

3.1.   Preoxidation-flotation separation test for mixed concentrate

3.1.1. Effect of H_2SO_4 concentration in preoxidation on flotation separation

The concentration of sulfuric acid affects the preoxidation processing and indirectly affects the flotation separation efficiency of copper-lead mixed concentrate. In this section, the effects of preoxidation acidity on the flotation separation of mixed concentrate were discussed at preoxidation temperature of 20 °C with reaction time of 30 min. The experiment procedure is shown in Fig. 2. The results from the flotation experiments for the preoxidation at different acidic concentration are shown in Fig 3.
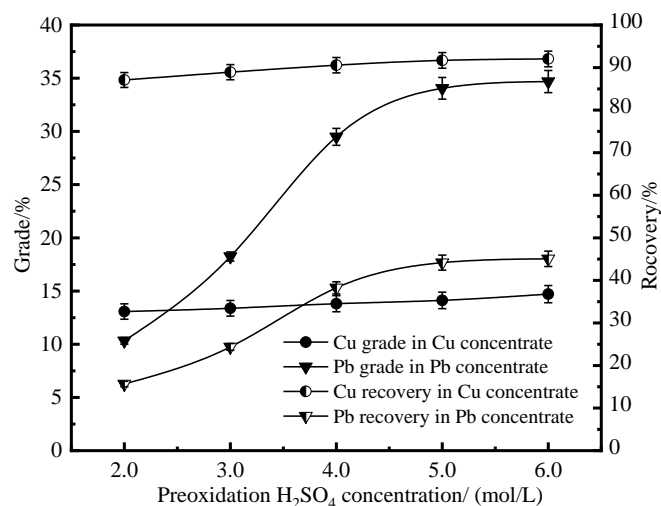

Fig. 3. Effect of H_2SO_4 concentration on flotation separation of copper-lead mixed concentrate

As shown in Fig. 3, with sulfuric acid concentration increasing from 2 mol/L to 6 mol/L during preoxidation of the mixed concentrate, Cu grade in flotation copper concentrate increased and tended to be stable, while Cu recovery is not significantly changed and keep higher than 90%. At the same time, the Pb grade in the lead concentrate increased from 10.32% to 34.69%, and the Pb recovery increased from 15.65% to 45.06%. The results showed that the flotation separation efficiency of copper and lead are improved with the increasing of preoxidation acidity. Therefore, the prefer concentration of sulfuric acid for the preoxidation was determined to be 5.0 mol/L in subsequent experiments.

3.1.2. Effect of preoxidation temperature on flotation separation

The preoxidation temperature affects the preoxidation reaction rate, and the surface preoxidation reaction rate will accelerate with the increase of temperature, which indirectly affects the flotation separation performance of copper-lead mixed concentrate. In this regard, the effects of preoxidation at different temperature on the flotation separation of mixed concentrate were evaluated. The experimental procedure and results are shown in Fig. 2 and Fig. 4 respectively.
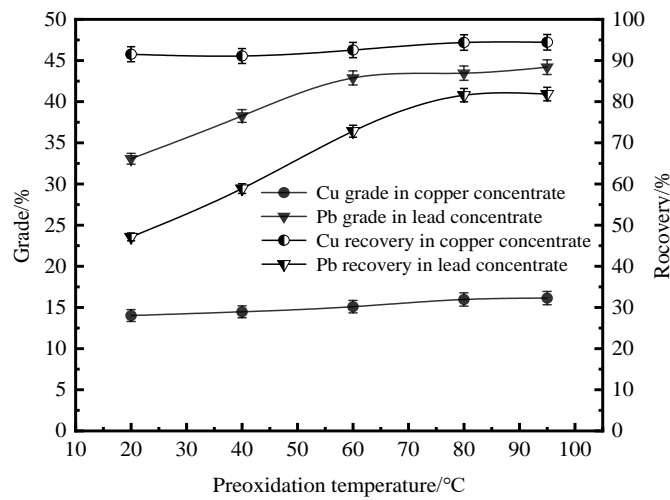

Fig. 4. Effect of preoxidation temperature on flotation separation of copper-lead mixed concentrate

From the results as shown in Fig 4, It can be see that with the preoxidation temperature increasing from 20 °C to 100 °C during preoxidation of mixed concentrate, the Cu grade in copper flotation concentrate is increased and tends to be stable with small fluctuate of Cu recovery above 90%. At the same time, the Pb grade in the lead concentrate increased from 32.06% to 44.19%, and the Pb recovery increased from 45.51% to 81.86%. The results showed that the flotation separation efficiency of copper and lead is significantly improved with the increasing of preoxidation temperature. Therefore, the preoxidation temperature was determined to be 100 °C in subsequent experiments.

3.1.3. Effect of preoxidation time on flotation separation

The preoxidation time affects the reaction degree of preoxidation process and then will affect the flotation separation efficiency. In this section, the effects of preoxidation at different reaction time on the flotation separation of mixed concentrate were discussed. The experimental procedure and results are shown in Fig. 2 and Fig. 5 respectively. It can be seen from Fig. 5 that with the preoxidation time increasing from 10 min to 50 min for the preoxidation process, the Cu grade in copper flotation concentrate increased and tended to be stable with small Cu recovery fluctuation above 90%. At the same time, the Pb grade in the lead concentrate increased from 16.53% to 43.51%, and the Pb recovery increased from 35.16% to 94.51%. The results showed that the flotation separation efficiency of copper from lead became better with the extension of preoxidation time. According to the flotation results , the preoxidation time was determined to be 40 min in subsequent experiments.

According to the peroxidation-flotation results of copper-lead mixed concentrate in Fig. 3 to Fig. 5 in Section 3.1, the Pb recovery and grade in Pb concentrate was significantly affected by the preoxidation

conditions, while the recovery of Cu in the Cu flotation concentrate was not significantly affected, indicating that floatability of galena in mixed concentrate is inhibited by peroxidation, while chalcopyrite's is not affected. Besides, we can preliminarily conclude that the perfer preoxidation conditions for copper-lead mixed concentrate were H2SO4 concentration 5 mol/L, temperature 100 °C, time 40 min. Under these conditions, a 17.83% of Cu concentrate with recovery of 94.11% and a 42.89% of Pb concentrate with recovery of 94.39% were obtained respectively.
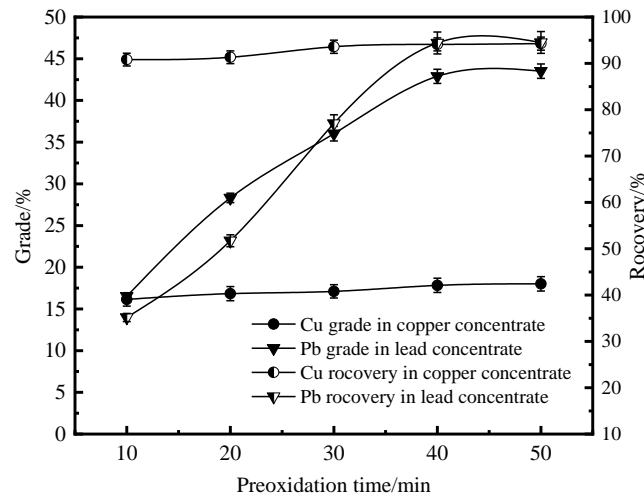

Fig. 5. Effect of preoxidation time on flotation separation of copper-lead mixed concentrate

3.2. FT-IR analysis

The study in Section 3.1 shows that the acid preoxidation can change floatability of copper and lead minerals in the mixed concentrates, and the flotation separation of copper and lead was significantly improved. In order to further understand the effect of acid proxidation on flotation, the surface oxidation status of copper and lead minerals was studied by FT-IR analysis. Infrared spectrum analysis results of chalcopyrite and galena samples are shown in Fig. 6 and Fig. 7. It can be seen from Fig. 6 that there are notable of -OH vibration peaks near 1636 cm-1 and 3450 cm-1 which are caused by the interaction of free water in the air with chalcopyrite surface. In a word, there are no pronounced characteristic peaks in the infrared spectra of the original chalcopyrite and the preoxidized chalcopyrite, indicating that the chalcopyrite is not significantly affected by sulfuric acid preoxidation. In addition, it also shows that the extension of preoxidation time has no significant effect on the preoxidation process of chalcopyrite.
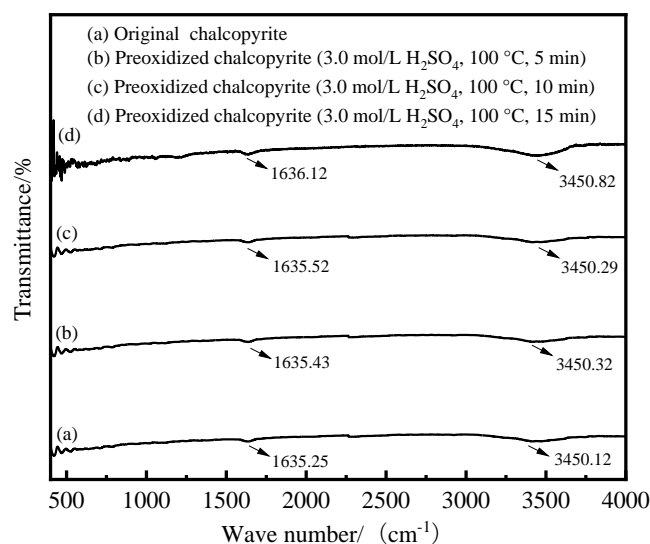

Fig. 6. Infrared spectrum analysis of chalcopyrite samples

On the other hand, it can be seen from Fig. 7 that there are notable of -OH vibration peaks near 1641 cm-1 and 3487 cm-1 which are caused by the interaction of free water in the air with galena surface. The peaks near 605 cm-1 and 1095 cm-1 are the characteristic peaks of sulfate (Cases and Donato. 1991), in which due to the electron absorption of oxygen ions, the stronger the double bond energy in the infrared spectrum, the more it will appear at the higher peak. So that it can be inferred that the absorption peak near 605 cm-1 is sulfite (SO_3^{2-}) and the absorption peak near 1095 cm-1 is sulfate (SO_4^{2-}). Moreover, with the enhancement of preoxidation conditions, the transmittance of sulfate and sulfite characteristic peaks around 605 cm-1 and 1095 cm-1 is also enhanced, indicating that the chemical adsorption of sulfate and sulfite on the mineral surface is also gradually enhanced and it is further indicated that the oxidation degree of galena is deepened with the increase of preoxidation time.
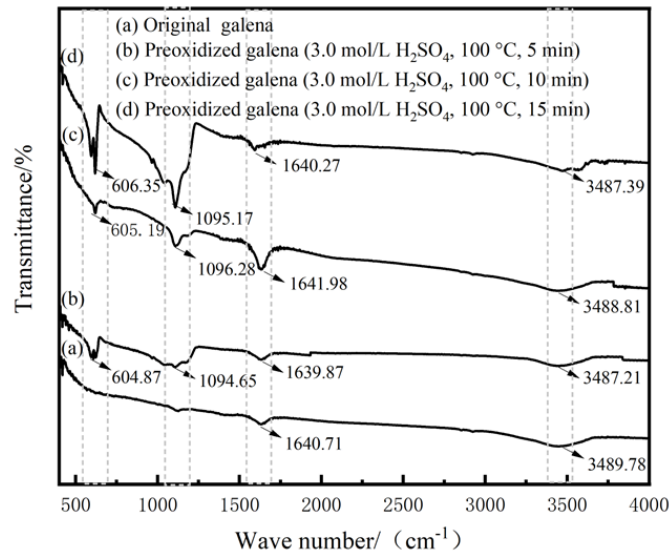
Fig. 7. Infrared spectrum analysis of galena samples

3.3. AFM analysis

In order to further investigate the surface composition of chalcopyrite and galena during preoxidation with sulfuric acid, the surface morphology and surface roughness of the two minerals were analyzed by AFM at the preoxidation sulfuric acid concentration of 3.0 mol/L, temperature of 100 ° and time of 20 min. The results are shown in Fig. 8 to Fig. 9.

3.3.1. AFM analysis of chalcopyrite

As shown in Fig. 8 (a) and Fig. 8 (c), there is no obvious change in the color of the surface topography area of the original chalcopyrite, indicating that no other substances are produced or attached to the surface. The surface of the original chalcopyrite exhibits a polycrystalline morphology composed of Cu, Fe, and S atoms, and the crystals are connected to each other to form a continuous sulfide film. It can be seen from Fig. 8 (b) that the surface roughness of the original chalcopyrite is 0.48 nm. As shown in Fig. 8 (d) and Fig. 8 (f), after chalcopyrite is preoxidized, the crystal part of the chalcopyrite surface is partially lost and the surface is partially sunken, indicating that sulfuric acid preoxidation will cause changes in the surface of chalcopyrite. In Fig. 8 (e) showed that the surface roughness of chalcopyrite is 11.03 nm. Combined with the FT-IR analysis above, there is no new material generated on the surface of chalcopyrite. It is speculated that under the action of sulfuric acid, the dissolution of Fe ion on the surface of chalcopyrite leads to the destruction of the crystal structure of chalcopyrite surface, the occurrence of lattice defects and etching cavities, resulting in the depression of chalcopyrite; at the same time, a passivation film with a thickness of about 1-10 nm was formed under the action of sulfuric acid, which was mainly composed of $Cu_{1-x}Fe_{1-y}S_{1-z}$ (y≫x, y+x≈1) (Klauber. 2008; Ghahremaninezhad, Dixon and Asselin. 2013; Ali and Ali. 2016). The original exposed surface was covered and the interior of chalcopyrite was protected, maintaining the hydrophobicity of chalcopyrite.
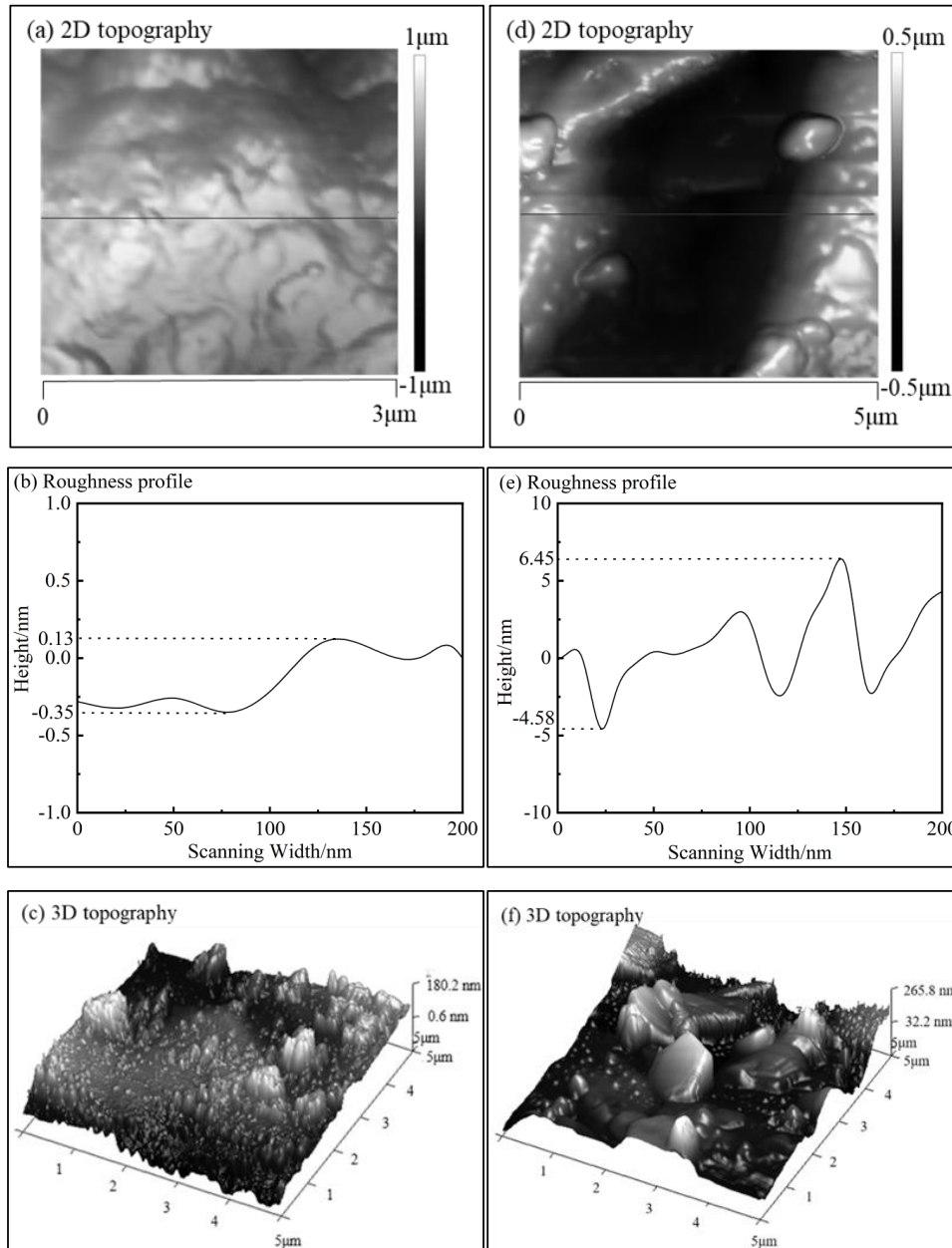
Fig. 8. AFM analysis of chalcopyrite samples

3.3.2. AFM analysis of galena

It can be seen from Fig. 9 (a), Fig. 9 (b) and Fig. 9 (c) that the surface roughness of the original galena is 0.39 nm, the surface morphology of the original galena shows the active action point of the dissociation surface fracture, and the regional color does not change significantly, indicating that there is no other material formation or adhesion on the surface and the polycrystalline morphology of PbS is presented on the surface, the crystals are interconnected and a continuous sulfide film is formed. As shown in Fig. 9 (d) and Fig. 9 (f), the surface of preoxidized galena is mostly highlighted thick lines, which are the boundary between different crystals (Luttrell and Yoon. 1984). As shown in Fig. 9 (e), the color of the area on the topography map changes obviously, in which the surface roughness is 18.51 nm and rougher than that of the original galena, it is speculated that new products will be produced or attached to the surface of preoxidized galena, and these new products are adsorbed on the surface of galena through the active action point of the galena dissociation surface. It will cover the original exposed surface, changing its surface properties while protecting the interior of galena, so that its surface hydrophobicity is changed.
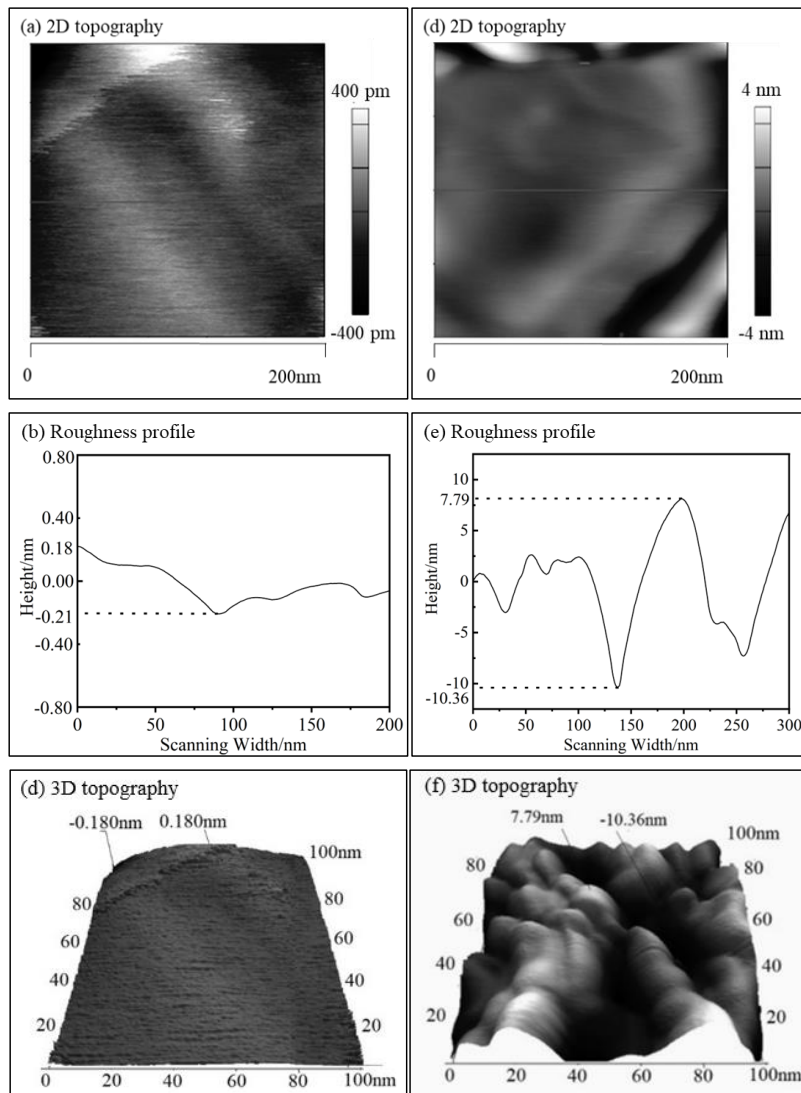
Fig. 9. AFM analysis of original galena and preoxidized galena

3.4. Mechanism analysis of sulfuric acid with galena and chalcopyrite

Previous studies have shown that the floatability of chalcopyrite preoxidized the action of sulfuric acid hardly changes under normal pressure. The academic community believes that this is mainly due to the release of Fe ions into the system after the action of chalcopyrite and sulfuric acid. Combining the results of FT-IR and AFM analysis, we can infer that the surface of chalcopyrite forms a passivation film dominated by $Cu_{1-x}Fe_{1-y}S_{1-z}$ ($y \gg x$, $y+x \approx 1$) and the interior of chalcopyrite is protected (Jin et al. 2022; Xie et al. 2021). Therefore, after the action of sulfuric acid, the surface composition of chalcopyrite is still a highly hydrophobic copper sulfide, which still has very good floatability. As for galena, under the action of sulfuric acid, the S^{2-} on the surface of galena undergoes redox reaction with oxygen to form S^0, and finally evolves into SO_4^{2-}, this part of the sulfate anion and SO_4^{2-} in solution combine with the positively charged lead ion Pb^{2+} on the mineral surface, so that the galena surface generates hydrophilic lead sulfate ($PbSO_4$), thus its floatability is reduced (Jin et al. 2022; Zhang et al. 2022; Xie et al. 2022). The mechanism of action of galena, chalcopyrite and sulfuric acid is shown in Fig. 10.

3.5. Peroxidation-flotation test parameter analysis and optimization

3.5.1. Analysis model design

Based on the results of the single factor experiments of peroxidation-flotation in Section 3.1, Response Surface Methodology (RSM) was adopted to design the test parameter analysis model. The sulfuric acid
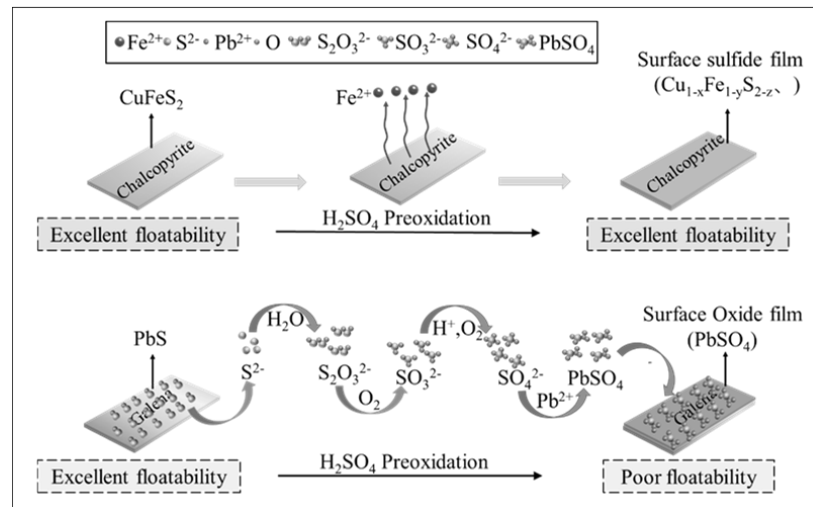
Fig. 10. Schematic diagram of preoxidation action mechanism of galena and chalcopyrite

concentration(X_1), preoxidation temperature(X_2), and preoxidation time(X_3) were selected as independent variables for the Box-Behnken module in Design Expert12. The Cu recovery in Cu concentrate and Pb recovery in Pb concentrate after preoxidation-flotation separation were taken as response values. The proposed design factors and central combination levels are shown in Table 5.

Table 5. The proposed design factors and central combination levels

Factors	Codes	Unit	Coding Levels		
			-1 (low)	0	1 (high)
H_2SO_4 concentration	X_1	mol/L	4	5	6
Preoxidation temperature	X_2	°C	90	100	110
Preoxidation time	X_3	min	30	40	50

3.5.2. Analysis of regression equation variance

The test scheme was generated by Design-Expert 12 software, and the test data was fitted by the method of multivariate quadratic regression response surface fitting. The quadratic regression equation models (see, E1 and E2) for Cu recovery in Cu concentrate and Pb recovery in Pb concentrate are shown in Eqs. (1) and (2):

$$E_1 = 94.73\% + 0.757X_1 + 0.453X_2 + 0.42X_3 - 0.573X_1X_2 + 0.053X_1X_3 -$$
$$- 0.103X_2X_3 - 1.08X_1^2 - 0.496X_2^2 - 0.251X_3^2 \tag{1}$$

$$E_2 = 94.24\% + 2.92X_1 + 1.70X_2 + 1.42X_3 - 0.073X_1X_2 + 0.753X_1X_3 -$$
$$- 0.265X_2X_3 - 4.73X_1^2 - 2.35X_2^2 - 1.38X_3^2 \tag{2}$$

Regression ANOVA was performed on the Cu recovery in Cu concentrate and Pb recovery in Pb concentrate model, and the results are shown in Table 6. Where the P-value represents the significance of the fitting model. When $P \leq 0.05$, it is significant, and $P \leq 0.0001$ indicates that the fitting model is highly significant (Yang et al. 2021). If the regression equation was favorable to the model, there is no defect, so the regression equation can be used to replace the experiment to analyze the experimental results.

As can be seen from Table 6, the Cu recovery regression model $P=0.048<0.05$ indicates that the Cu recovery model is significant and can be used for response prediction and analysis. Besides, the P values of the factors X_1, X_2, X_3 and the secondary terms X_1^2, X_3^2 and are less than 0.05, indicating that the Cu recovery in Cu concentrate is significantly affected by X_1, X_2, X_3, X_1^2, X_2^2 and X_1X_2. The Pb recovery regression model $P<0.0001$ indicates that the Pb recovery model is highly significant and can be used for response prediction and analysis. Moreover, the P values of the factors X_1, X_2, X_3 and the secondary terms X_1^2, X_2^2 and X_3^2 are less than 0.05, indicating that the Pb recovery in Pb concentrate is significantly affected by X_1, X_2, X_3, X_1^2, X_2^2 and X_3^2.

Table 6. Regression variance analysis of Cu recovery and Pb recovery model

Products	Cu recovery in Cu concentrate (%)			Pb recovery in Pb Concentrate (%)		
Source	Coefficient	F-value	P-value	Coefficient	F-value	P-value
Model	94.73	8.65	0.0048	94.24	33.57	<0.0001
X_1	0.757	22.76	0.002	2.92	83.86	<0.0001
X_2	0.453	8.12	0.0247	1.70	28.50	0.0011
X_3	0.42	7	0.0332	1.42	19.69	0.0030
X_1X_2	-0.573	6.5	0.0381	-0.073	0.026	0.8769
X_1X_3	0.053	0.0547	0.8218	0.753	2.78	0.1394
X_2X_3	-0.103	0.2084	0.6619	-0.265	0.345	0.5755
X_1^2	-1.08	24.41	0.0017	-4.73	115.55	<0.0001
X_2^2	-0.496	5.14	0.0577	-2.35	28.56	0.0012
X_3^2	-0.251	1.32	0.2887	-1.38	9.86	0.01639

3.5.3. Evaluation of influencing factors

In order to further study the interaction between various factors in the preoxidation test and determine the optimal preoxidation conditions for flotation separation of copper-lead mixed concentrate, the response surface analysis of the regression model was carried out by Design Expert 12 software, and the contour plot and 3D surface plot of sulfuric acid concentration, preoxidation temperature and time on the Cu recovery in Cu concentrate and the Pb recovery in Pb concentrate were obtained, as shown in Fig. 11 and Fig. 12 (a), (b), and (c), respectively.

It can be seen from Fig. 11 that the Cu recovery in Cu concentrate is not significantly affected by preoxidation acidity, temperature and time, and it is weakly affected by the interaction between various factors. After preoxidized by sulfuric acid, the surface composition of chalcopyrite is still a highly hydrophobic copper sulfide, which still has very good floatability. The results of this study further confirm these results and the effect of sulfuric acid preoxidation on the Cu recovery in Cu concentrate is minimal. Combined with the characteristics of contour and 3D surface plot of Fig. 11 (a), (b) and (c), the significant effects of various factor and their interaction on the Cu recovery in Cu concentrate is in the order of $X_1>X_2>X_3>X_1X_2＞X_2X_3＞X_1X_3$.

From Fig. 12(a) and Fig. 12(b), it can be seen that when the preoxidation sulfuric acid concentration is 5 mol/L, increasing the temperature and extending the time can increase, the Pb recovery in Pb concentrate, and the curve corresponding to the preoxidation temperature is relatively steep, indicating that the influence of preoxidation temperature on the Pb recovery in Pb concentrate is more significant than that of preoxidation time. It can be seen from Fig. 12(b) and Fig. 12(c) that when the preoxidation time is 30 min, the Pb recovery in Pb concentrate increases sharply with the increase of sulfuric acid concentration. But with the increase of preoxidation temperature, the Pb recovery in Pb concentrate shows a trend of first increasing and then decreasing. The increase is smaller than that when changing the sulfuric acid concentration, indicating that the effect of preoxidation acidity on the Pb recovery in Pb concentrate is more significant than the temperature. Combined with the characteristics of contour and 3D surface plot of Fig. 12 (a), (b) and (c), the significant effects of various factors and their interaction on the Pb recovery in Pb concentrate is in the order of $X_1>X_2>X_3＞X_1X_3＞X_2X_3＞X_1X_{2..}$.

The correlation coefficients of the Cu recovery in Cu concentrate and Pb recovery in Pb concentrate fitting equations are $R_1^2=0.9175$ and $R_2^2=0.9774$ respectively, indicating that the Cu recovery model can explain the response change of 91.75% and the Pb recovery model can explain the change of response value of 97.94%，indicating that the established model is reliable and can effectively predict the results.

### 3.6. Optimization and validation of preoxidation-flotation of copper-lead mixed concentrate

The optimal test conditions by RSM for the preoxidation of copper-lead mixed concentrate were sulfuric acid concentration of 5.3 mol/L, temperature of 101.8 °C and time of 48.3 min. It was predicted that the
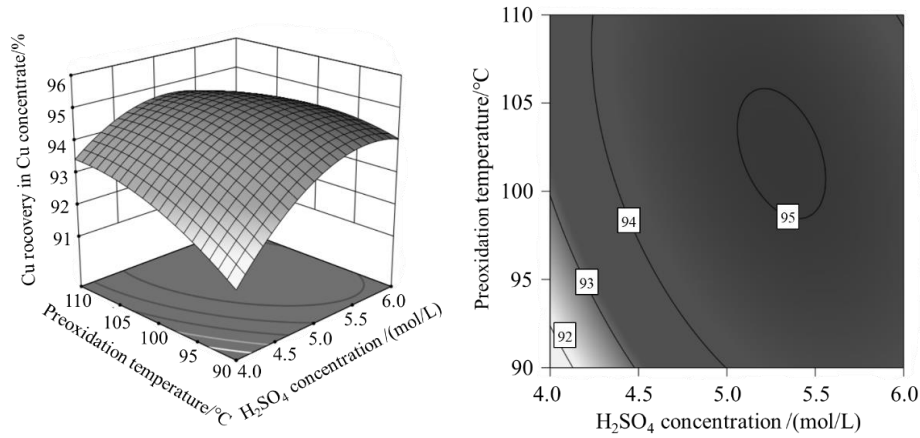
(a) Response surface and contour map of preoxidation acidity-temperature
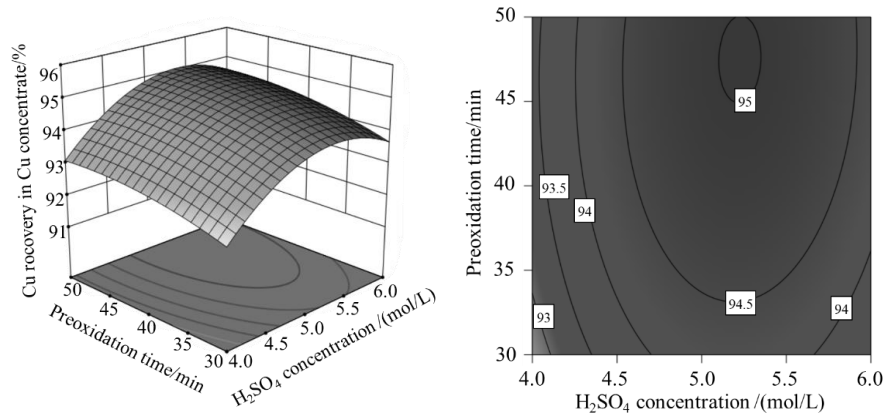
(b) Response surface and contour map of preoxidation acidity-time
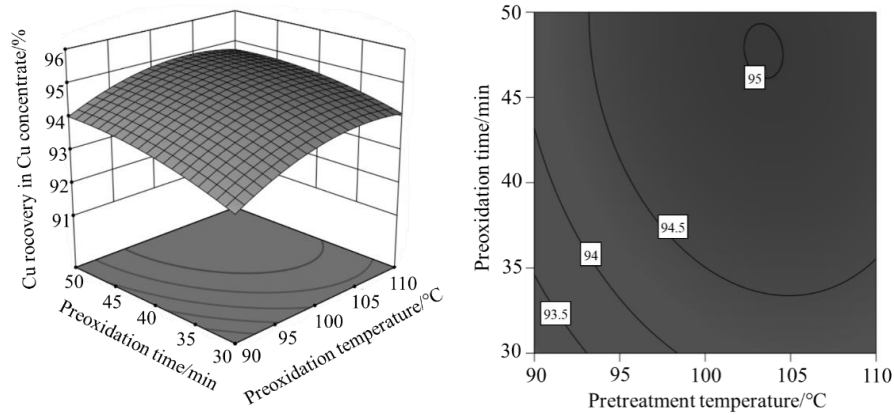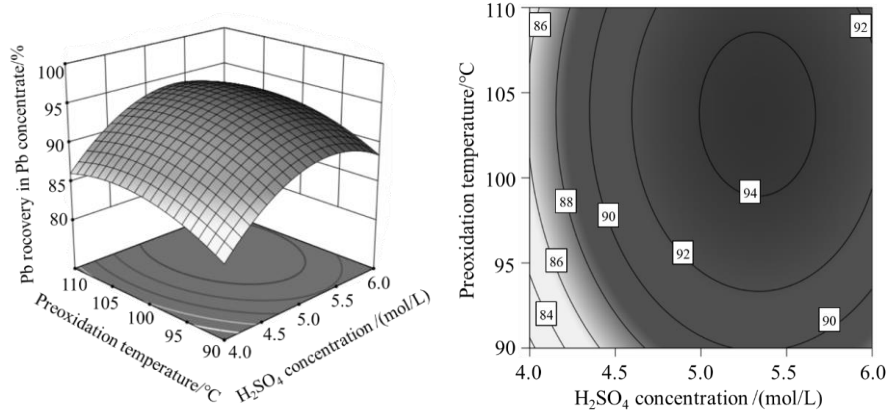

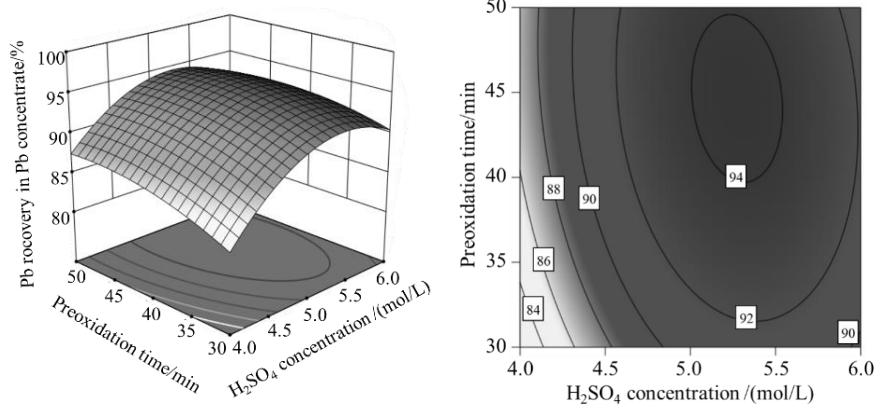(c) Response surface and contour map of preoxidation temperature-time

Fig. 11 Response surface diagram of the interaction of various factors on Cu recovery

Cu recovery in Cu concentrate and Pb recovery in Pb concentrate was 95.06% and 94.90% by flotation after the above preoxidation conditions. Under the above optimized preoxidation parameters, the flotation separation experiment of copper-lead mixed concentrate was carried out to verify the accuracy of the analysis model. The test flowsheet is shown in Fig. 13, and the test results are shown in Table 7.

As can be seen from the results in Table 7, the Cu concentrate with Cu grade of 18.09% and recovery of 95.41%, and Pb concentrate with Pb grade of 44.96% and recovery of 95.94% were obtained respectively. The relative error of Cu recovery was 0.35% and 1.04% of Pb recovery compared with the predicted value, indicating that the established model was reliable, which can effectively optimize the preoxidation-flotation separation conditions of copper-lead mixed concentrate, and further can be used to guide the improvement of copper lead separation index.

(a) Response surface and contour map of preoxidation acidity- temperature

(b) Response surface and contour map of preoxidation acidity-time
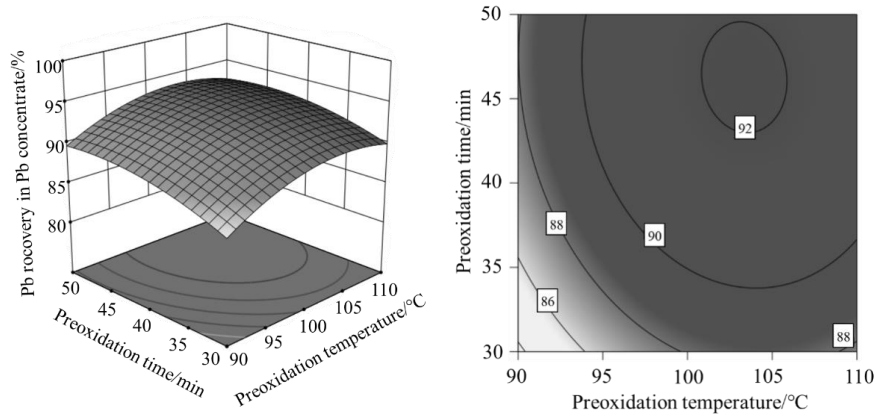
(c) Response surface and contour map of preoxidation temperature-time

Fig. 12. Response surface diagram of the interaction of various factors on Pb recovery

Table 7. Results of preoxidation-flotation separation of copper-lead mixed concentrate

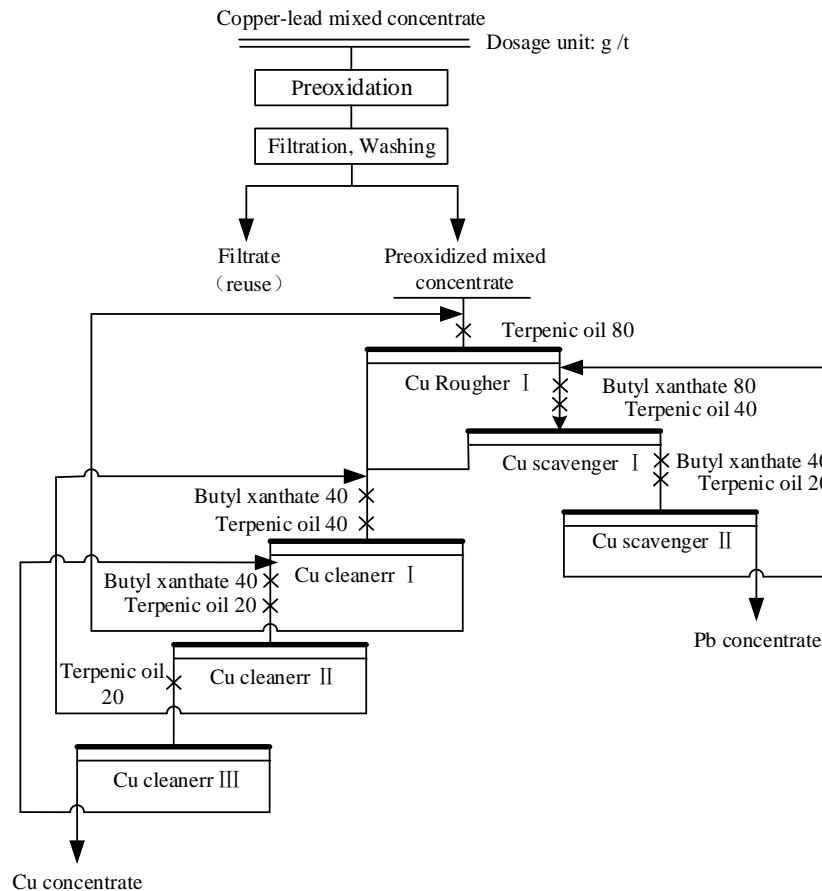| Product	Productivity	Grade/%		Recovery/%	
		Cu	Pb	Cu	Pb
Cu concentrate	62.93	18.09	1.12	95.41	4.06
Pb concentrate	37.07	1.48	44.96	4.59	95.94
Preoxidized mixed Concentrate	100.00	11.93	17.37	100.00	100.00

Fig. 13. The flowsheet of preoxidation-flotation separation for copper-lead mixed concentrate

4. Conclusions

In this paper, a new process of peroxidation-flotation separation of galena and chalcopyrite was developed. When sulfuric acid was used as the preoxidant, FT-IR and AFM analysis results showed that the surface of galena was oxidized and changed from hydrophobic to hydrophilic, which effectively reduced the galena floatability. However, sulfuric acid had little effect on the hydrophobicity of chalcopyrite, and it still maintained good floatability. During peroxidation, sulfuric acid concentration ($X1$), temperature ($X2$) and time ($X3$) had significant influence on flotation separation effect of copper-lead mixed concentrate. The analysis and optimization results of the three parameters by RSM method showed that the importance of influencing factors was in the order of $X1>X2>X3$, and the optimal parameters of preoxidation of copper-lead mixed concentrate were sulfuric acid concentration of 5.3 mol/L, the temperature of 101.8 °C and the time of 48.3 min. The flotation separation test was carried out after preoxidation under the above conditions, and the recovery rate of Cu in copper concentrate and Pb in lead concentrate was 95.41% and 95.94% respectively. The new peroxidation-flotation method provides a potential application prospect for the high-efficiency separation of copper-lead mixed concentrate.

Acknowledgement

References

ALI R., ALI D., 2016. *Electrochemical Characterization of Natural Chalcopyrite Dissolution in Sulfuric Acid Solution in Presence of Peroxydisulfate*. Electrochimica Acta. 212, 921-928.

BAI R., WEI Z., PENG R., WANG H., 2021. *Research status and progress of flotation separation of copper-lead sulfide minerals.* Conservation and Utilization of Mineral Resources. 41, 74-79.

CHEN, H., CUI Y., TONG X., 2016. *Research status and development of copper and lead separation in the sulfide ores*. Mining and Metallurgy. 25, 13-16.

CHERNYSHOVA I., ANDREEV S., 1997. *Spectroscopic study of galena surface oxidation in aqueous solutions I. Identification of surface species by XPS and ATR/FTIR spectroscopy.* Applied Surface Science. 108, 225-236.

CASES J., DONATO P., 1991. *FTIR analysis of sulphide mineral surfaces before and after collection: galena.* International Journal of Mineral Processing. 33, 49-65.

DUAN S., YANG S., JIANG Y., 2022. *Experimental study on separation bulk concentrate containing gold, copper and lead*. Nonferrous Metals (Mineral Processing Section). 5, 100-106+136.

FEN J., CUI Y., WANG D., HU C., 2021. *Research of the replacement of dichromate with depressants mixture in the separation of copper-lead sulfides by flotation.* Separation and Purification Technology. 278, 119330.

GHAHREMANINEZHAD A., DIXON D., Asselin E., 2013. *Electrochemical and XPS analysis of chalcopyrite (CuFeS2) dissolution in sulfuric acid solution.* Electrochimica Acta. 87, 97-112.

JIN Y., XIE H., ZHANG P., CHEN J., ZENG P., FENG D., LIU D., 2022. *Optimization of surface modification parameters of galena based on response surface methodology.* Nonferrous Metals Engineering. 12, 117-124.

JIN Y., XIE H., ZHANG P., LIU Y., RAO B., FENG D., JI C., 2022. *A study on characteristics and mechanism of surface passivation of galena in the presence of sulfuric acid*. Journal of Minerals. 42, 343-350.

KE B., CHEN J., 2022. *Influence of galvanic interaction between chalcopyrite and galena on electrochemical and flotation behaviour of chalcopyrite.* Applied Surface Science. 573, 151475.

KLAUBER C. 2008. *A critical review of the surface chemistry of acidic ferric sulphate dissolution of chalcopyrite with regards to hindered dissolution*. International Journal of Mineral Processing. 86, 1-17.

LAI H., LIU Q., DENG J., WEN S., LIU Z., 2020. *Surface chemistry study of Cu-Pb sulfide ore using ToF-SIMS and multivariate analysis.* Applied Surface Science. 518, 146270.

LEIRO J., TORHOLA M., LAAJALEHTO K., 2017. *The AFM method in studies of muscovite mica and galena surfaces.* Journal of Physics and Chemistry of Solids. 100, 40-44.

LIANG Z., LI G., WEI Z., WU W., HUANG X., WANG J., CUI L., NI X., ZHONG S., 2021. *Replacing Dichromate with Polysaccharide Depressant in Cu-Pb Separation: Lab Bench Tests and Plant Trials in Zijin Mining*. Mining, Metallurgy & Exploration. 38, 5.

LIU M., ZHANG C., HU B., SUN Z., XU Q., WEN J., XIAO J., DONG Y., GAN M., SUN W., ZHU J., CHEN D., 2020. *Enhancing flotation separation of chalcopyrite and galena by the surface synergism between sodium sulfite and sodium lignosulfonate.* Applied Surface Science. 507, 145042.

LUTTRELL G., YOON R., 1984. *The collectorless flotation of chalcopyrite ores using sodium sulfide*. International Journal of Mineral Processing. 13, 271-283.

MA Y., HAN Y., ZHU Y., LI Y., LIU H., 2016. *Flotation behaviors and mechanisms of chalcopyrite and galena after cyanide treatmen.* Transactions of Nonferrous Metals Society of China 26, 3245-3252.

NAGARAJ D., FARINATO R., 2016. *Evolution of flotation chemistry and chemicals: A century of innovations and the lingering challenges.* Minerals Engineering. 96, 2–14.

OCTOBER L., CORIN K., MANONO M., SCHREITHOFER N., WIESE J., 2020. *A fundamental study considering specific ion effects on the attachment of sulfide minerals to air bubbles.* Minerals Engineering. 151, 106313.

PATRA P., NATARAJAN K., 2008. *Microbially-induced separation of chalcopyrite and galena*. Minerals Engineering. 21, 691-698.

QIU T., YAN H., LI J., LIU Q., AI G., 2018. *Response surface method for optimization of leaching of a low-grade ionic rare earth ore.* Powder Technology. 330, 330-338.

RAHDAR S., PAL K., MOHAMMADI L., RAHDAR A., GOHARNIYA Y., SAMANI S., KYZAS G., 2021. *Response surface methodology for the removal of nitrate ions by adsorption onto copper oxide nanoparticles*. Journal of Molecular Structure. 1231, 129686.

SOMAYEH R., PAL K., MOHAMMADI L., RAHDAR A., GOHARNIYA Y., SAMANI S., KYZAS G., 2021. *Response surface methodology for the removal of nitrate ions by adsorption onto copper oxide nanoparticles*. Journal of Molecular Structure. 1231, 129686.

SRDJAN M., 2007. 15-Flotation of Copper–Lead–Zinc Ores. Elsevier. 367-400.

SUBRAMANIAN S., SANTHIYA D., NATARAJAN K., 2003. *Surface modification studies on sulphide minerals using bioreagents*. International Journal of Mineral Processing. 72, 175-188.

SUN W., DAI S., ZHANG H., CHEN Y., YU X., LI P., LIU W., 2022. *Selective flotation of chalcopyrite from galena using a novel collector benzoic diethylcarbamothioic thioanhydride: An experimental and theoretical investigation*. Journal of Molecular Liquids. 365, 120027.

SU C., LIU D., SHEN P., CAI J., YANG S., 2020. *Research progress on electrochemical characteristics and flotation behavior of chalcopyrite and galena*. Nonferrous Metals Engineering. 10, 79-87.

WANG X., QIN W., JIAO F., LIU R., WANG D., 2019. *Inhibition of galena flotation by humic acid: Identification of the adsorption site for humic acid on moderately oxidized galena surface.* Minerals Engineering. 137, 102-107.

WANG Y., XIONG W., ZHANG X., LU L., ZHU Y., 2021. *A new synthetic polymer depressant PADEMA for Cu-Pb separation and its interfacial adsorption mechanism on galena surface*. Applied Surface Science. 569, 151062.

XIE H., WU J., TIAN X., XIAO W., LIU R., GAO L., TONG X., 2019. *Selective flotation separation of copper-zinc-sulfur bulk concentrate.* Journal of Mineralogy. 39, 1-6.

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.* Separation and Purification Technology. 267, 118621.

XIE H., JIN Y., ZHANG P., LIU Y., GAO L., FENG Q., LIU D., 2022. *Surface modification mechanism of galena with H2SO4 and its effect on flotation separation performance.* Applied Surface Science. 579, 152129.

YANG S., LIU D., ZHUANG G., CAI J., SU C., LI J., 2021. *Optimization of leaching process of fine copper oxide by response surface methodology*. China Mining. 30, 128-133.

ZHANG P., XIE H., JIN Y., LIU Y., TANG D., FENG D., 2022. *Study on new technology of high efficient separation of copper-lead sulfide mixed concentrate.* Nonferrous Metals Engineering. 12, 96 -103.

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*. Minerals Engineering. 134, 291-299.

ZHANG P., XIE H., JIN Y., CHEN J., ZENG P., LIU D., TONG X., 2022. *Optimization analysis of a new surface efficient separation process for copper-lead sulfide ore by Response surface methodology*. Journal of Kunming University of Science and Technology (Natural Science). 47, 40-50.