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Synergistic effect between starch and sulfuric acid the separation of galena from chalcopyrite

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Abstract: Galena (PbS) is still hard to separate from chalcopyrite ($CuFeS_2$) in China, necessitating more effective depressants. This study investigated a combined depressant system using sulfuric acid (H_2SO_4) and starch to selectively depress PbS in a PbS−$CuFeS_2$ mixture. Single-mineral flotation experiments identified the optimal parameters to depress PbS at pH 3, 6 min reaction time, an H_2SO_4 to starch ratio of 6:1, and 700 mg/dm^3 of H_2SO_4. Under these conditions, PbS recovery has decreased to 9.2%, while $CuFeS_2$ recovery reached 81.1%, Furthermore, the PbS recovery with this combined depressant was significantly lower than the recovery with 700 mg/dm^3 of H_2SO_4 (83.2%) or 116.7 mg/dm^3 of starch (32.1%). FTIR results also showed that starch molecules could physically adsorb onto the PbS surface. Furthermore, XPS and SEM-EDS analyses revealed that the interaction between H_2SO_4 and the PbS surface produced oxidative components, i.e., Pb-O and SO_4^{2-}. These oxidative species may interact with the OH groups in starch molecules, enhancing the adsorption of starch molecules and thus efficiently producing a hydrophilic PbS surface. This study proposes an effective approach for the depression of PbS using the H_2SO_4 and starch combination. These combined reagents exhibit outstanding industrial potential, owing to their low prices.

Keywords: galena depression, combined depressants, flotation, hydrophobicity, starch

1. Introduction

Chalcopyrite ($CuFeS_2$) remains the major source of copper (Wei et al., 2020; Zhang et al., 2020). The $CuFeS_2$ flotation attracts growing attention, since copper is widely used in power, construction, transportation, machinery, and manufacturing (Cruz-Cruz et al., 2024; Ma et al., 2008; Tang et al., 2025; Xu et al., 2024). $CuFeS_2$, galena (PbS), and sphalerite (ZnS), are commonly coexist in deposits of China (Kordloo et al., 2024; Shen et al., 2024). ZnS is ready to be separated from other sulfides using sodium carbonate (Na_2CO_3) and zinc sulfatezinc sulfate ($ZnSO_4$) (Sun et al., 2022; Zhang et al., 2021). Whereas the flotation behaviors of $CuFeS_2$ and PbS are similar to each other, and thus it is relatively hard to separate these two minerals. Additionally, dissolved Cu^{2+} and Pb^{2+} ions can adsorb on the surfaces of PbS or $CuFeS_2$, leading to the activation of both minerals (Irannajad et al., 2019; Wang et al., 2021).

Commonly, as for the PbS and $CuFeS_2$ system, a depressant was employed to prevent the PbS or $CuFeS_2$. Sodium cyanide (NaCN) is a traditional depressant for $CuFeS_2$; however, its application has been diminished in plants due to its high toxicity. Other reported depressants for $CuFeS_2$ include dichromate (He et al., 2023), potassium permanganate (Li et al., 2018), sulfite (Liu et al., 2020; Pan et al., 2022), and sodium sulfide (Na_2S). Nonetheless, there are limited studies on $CuFeS_2$ depressants, as $CuFeS_2$ is challenging to depress due to the stability of its surface.

Significant research has focused on PbS depressants, resulting in the development of numerous organic depressants that are non-toxic and biodegradable. These organic reagents include dextrin (Garcia et al., 2008), starch (Yang and Wang, 2018), humates (Dong et al., 2022), lignin, and sodium

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pyrophosphate (Qin et al., 2012). Polysaccharide-based macromolecular depressants have been utilized in mineral processing for nearly seventy years, primarily as flocculants and depressants in iron ore processing (Cao et al., 2024a; Nagaraj and Farinato, 2016; Ran et al., 2023). Starch, being relatively inexpensive compared to other organic depressants, is the most prevalent natural polysaccharide used in mineral processing.

Sulfuric acid (H_2SO_4) has recently been identified as a highly effective depressant for PbS (Xie et al., 2021a). H_2SO_4 offers the advantages of wide availability and low cost since many non-ferrous mines are capable of producing H_2SO_4 by themself. However, the application of H_2SO_4 suffers from several factors, including a high dosage (2.0 mol/dm^3), extended reaction time (15 min), and elevated slurry temperature (100°C) (Jin et al., 2024). These limitations cause challenges for the industrial utilization of H_2SO_4, highlighting the necessity for alternative methods to enhance its depressant capabilities. In recent years, the combination of organic and inorganic reagents has attracted significant attention. This type of depressant combination has been shown to substantially reduce the required dosage compared to individual reagents, and the synergy created by this combined approach can enhance the overall depression effect (Jin et al., 2023; Liu et al., 2017). In recent years, the combination of organic and inorganic reagents has attracted significant attention. The combination of sodium phytate and sodium silicate produces a synergistic effect, resulting in significantly enhanced inhibition of dolomite (Chen et al., 2025). Fe^{3+} enhances the adsorption of tartaric acid onto the calcite surface, thereby strengthening its depressant effect on calcite (Dong et al., 2021). It is reasonable to anticipate that a combination of H_2SO_4 and organic reagents may also produce a synergistic effect, potentially lowering the H_2SO_4 dosage. However, to date, there has been no reported research on the interplay between H_2SO_4 and organic reagents, such as starch.

The objective of the present work is to evaluate the depressant abilities of H_2SO_4 and starch on the PbS flotation. The optimal conditions for PbS depression using a combination of these depressants were first explored through flotation experiments. Subsequently, the contact angle experiments were carried out to assess the hydrophobicity depletion of the PbS surface treated by the H_2SO_4 and starch solution. Fourier-transform infrared spectroscopy (FTIR) was employed to probe the starch adsorption state on the mineral surfaces. Furthermore, the chemical states of elements on the mineral surfaces were compared using X-ray photoelectron spectroscopy (XPS). In addition, the distribution properties of elements on PbS and $CuFeS_2$ surfaces were determined with scanning electron microscopy and Energy-dispersive X-ray spectroscopy (SEM−EDS).

2. Materials and methods

2.1. Materials

$CuFeS_2$/PbS samples were hand-picked from a multiple-sulfide ore in Yunnan Province, China. Results of XRD and XRF analyses of the samples were already illustrated in a previous paper (Zhang et al., 2025). The purity of the samples meets the needs of the tests. The samples were ground dry to obtain different size fractions. The 0.074-0.037 mm fraction was utilized in the flotation tests, and the -0.037 mm fraction was employed in FTIR and XPS analysis.

The starch was procured from Sigma Aldrich. The structure of starch molecule is displayed in Fig. 1. Pine oil obtained from Zhuzhou Sanlin Chemicals Ltd. was used as a frother. Analytically pure H_2SO_4 was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Reagents included analytically pure starch and H_2SO_4 (Shanghai Aladdin Biochemical Technology Co., Ltd.), with pH adjusted using diluted HCl and NaOH solutions. Deionized (DI) water (Milli-Q EQ 7000, 18 MΩ•cm^{-1}) was used for all experiments at 23 °C.

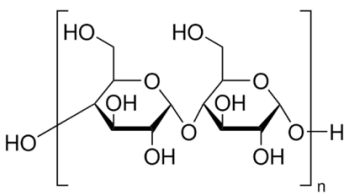

Fig. 1. Molecular formula of soluble starch

2.2. Methods

2.2.1. Minerals and reagents

PbS and $CuFeS_2$ sourced from Huize County, Yunnan Province, China. XRD results (Fig. 2) indicated exclusive presence of PbS and $CuFeS_2$. XRF analysis (Table 1) revealed a Pb grade of 87.12% in the PbS sample and a Cu grade of 38.91% in the $CuFeS_2$ sample.

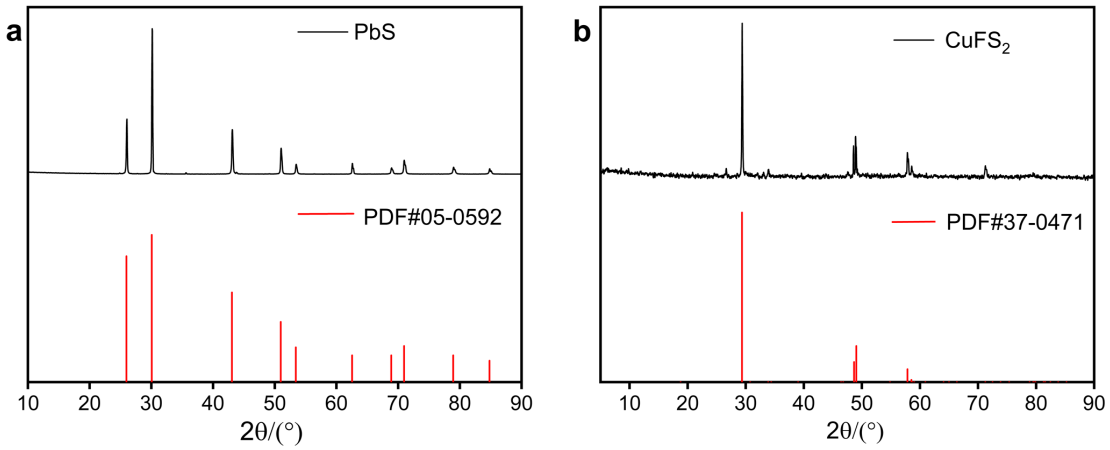

Fig. 2. XRD patterns of PbS and $CuFeS_2$. The standard PDF cards of PbS and $CuFeS_2$ are plotted in the figure

Table 1. XRF results for the mineral samples (wt.%)

Mineral	Cu	Fe	S	Zn	Al	Si	Pb	Sb
Galena	-	0.07	12.81	-	-	-	87.12	-
Chalcopyrite	38.91	30.54	29.69	0.60	0.09	0.04	0.05	0.08

2.2.2. Flotation experiments

Flotation experiments were conducted with 2 g of mineral in XFGC II flotation machine (Jilin Province Ore Exploration Machinery Factory, Changchun, China) and a 40 cm^3 flotation cell. H_2SO_4 and starch solutions were also added to the flotation cell. Subsequently, pine oil was introduced to the flotation cell. The impeller speed during the flotation tests was maintained at 1970 rpm, and air flow rate was regulated at 0.67 LPM. The concentrate and tailings products were then collected to calculate the recovery. In addition, each test was repeated three times. The maximum experimental error in the flotation tests was ± 2%.

2.2.3. Contact angle measurements

A GBX Contact Angle Meter (France) was employed to measure the contact angles of the samples using the sessile droplet method. Pure PbS and $CuFeS_2$ crystals (20 mm × 15 mm) were used in the measurements. The crystal surface was polished using sandpapers (4000 and 6000 grit) before the measurements. Then, the crystals were conditioned by 100 cm^3 of H_2SO_4 and starch for 6 min. Further, the crystal was gently flushed with DI water and dried in air, after which a water droplet (2-3 mm in diameter) was induced onto the PbS or $CuFeS_2$ surface. A camera was used to record the droplet images for the contact angle measurements. The error of the contact angle measurements was less than ± 2°.

2.2.4. FTIR analysis

FTIR spectroscopy analyses were performed by a Nicolet IS50 (Thermo Fisher Scientific, Waltham, MA, USA) in the region of 4000-500 cm^{-1}. PbS or $CuFeS_2$ (1 g) was reacted with 100 cm^3 of H_2SO_4/starch solution in a beaker. The slurry was conditioned for 6 min (500 rpm). Furthermore, the mineral sample was further filtered and dried under vacuum. 10 mg of dry sample and 100 mg of KBr were well blended in an agate mortar. The whole powder sample was compressed to a disk for the FTIR study.

2.2.5. XPS analysis

X-ray photoelectron spectroscopy (XPS) analysis was performed using a PHI5000 system (Thermo Fisher Scientific, USA) equipped with a monochromated Al Kα X-ray source. Moreover, the XPS spectra were fitted by MultiPak spectroscopy software. Meanwhile, the standard binding energy of the C 1s peak was employed to calibrate the spectra. A total of 1.0 g of pure PbS or $CuFeS_2$ was immersed in a 100 cm^3 solution of combined depressants. The reaction time crystal with the reagent solution was 6 min.

2.2.6. SEM-EDS analyses

SEM-EDS analyses were performed utilizing a Tescan Mira 4 instrument (TESCAN MIRA, Czech Republic) using 15 kV and a current of 300 pA. The PbS or $CuFeS_2$ particles (2 g) were reacted with 100 cm^3 of H_2SO_4 and starch solution for 3 min. Furthermore, the sample was filtered for the SEM analysis. Besides, the surfaces of natural samples were also measured for comparison. It should be mentioned that the god sputter-coating method was employed to improve the conductivity of the mineral samples.

3. Results and discussion

3.1. Depressing ability of the combined depressants

This section investigates the depressing behavior of the H_2SO_4/starch depressants for PbS flotation using the flotation experiments. The optimal parameters for the H_2SO_4 and starch mixture were also determined, including the depressant dosage, the mole ratio of H_2SO_4: starch, and the reaction time of the depressant mixture.

3.1.1. Effect of H_2SO_4 and starch reagent concentration

Firstly, the influence of H_2SO_4 or starch dosage on the flotation behavior of PbS and $CuFeS_2$ was evaluated as illustrated in Fig. 3. The reaction time for H_2SO_4 or starch was set as 6 min in the flotation experiments. When the H_2SO_4 dosage was increased from 50 to 250 mg/dm^3, the PbS recovery notably declined, dropping to 9.2% with 250 g/dm^3 H_2SO_4. A similar dosage of H_2SO_4 was required to inhibit the PbS flotation in a previous work (Cao et al., 2024b). As for $CuFeS_2$, its recovery remained relatively stable within the entire range of H_2SO_4 concentration (50-250 g/dm^3). The $CuFeS_2$ recovery still reached 80.3% even with 250 g/dm^3 H_2SO_4. It seems that the H_2SO_4 treatment barely lowered the floatability of $CuFeS_2$, which is in agreement with a previous report (Feng et al., 2021).

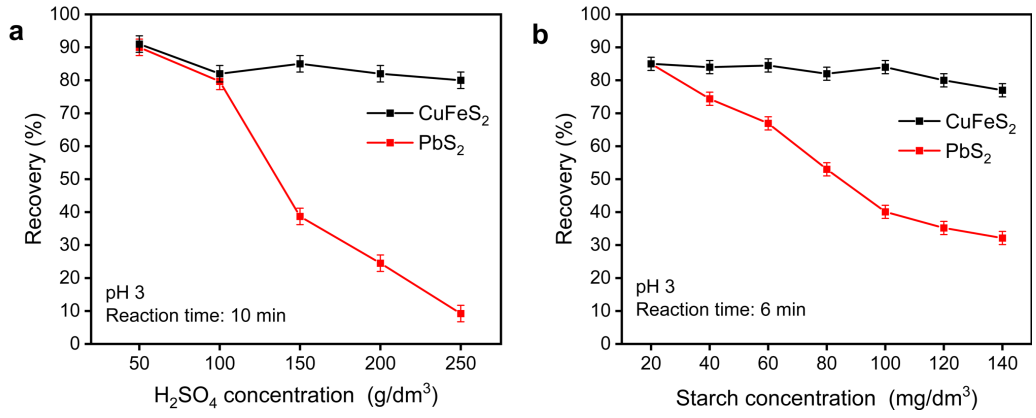

Fig. 3. Flotation behaviors of PbS and $CuFeS_2$ depending on the H_2SO_4 (a) and starch concentrations (b)

Previous work showed that starch could depress PbS in an acidic slurry. While the natural pH of dilute H_2SO_4 and starch solution was pH 3 as measured in this work and the change in starch concentration did not change the solution pH. It was found that the PbS recovery was decreased as the starch dosage increased. Specifically, the PbS recovery was only 32.1% treated by 140 mg/dm^3 of starch. On the contrary, the $CuFeS_2$ recovery reached 77.2% with 140 mg/dm^3 of starch. This result means that starch could be a depressant for PbS rather than $CuFeS_2$.

The above results show that both H_2SO_4 and starch can be used as specific depressants for PbS. While 250 g/dm^3 of H_2SO_4 was needed to prevent PbS flotation. Starch showed a stronger depressing capacity, but 140 mg /dm^3 starch was still required.

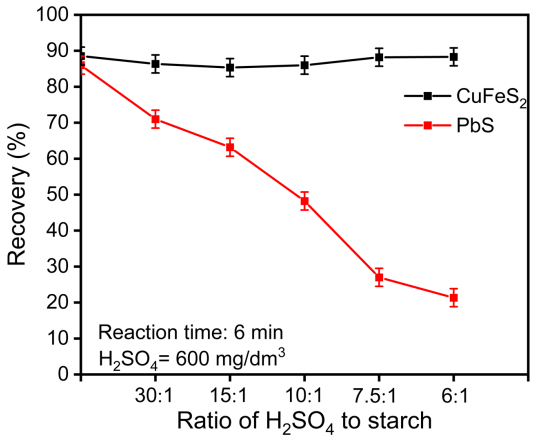

Fig. 4. Flotation recoveries of PbS and $CuFeS_2$ relying on the ratio of H_2SO_4 to starch at pH 3

Moreover, the H_2SO_4 and starch mixture was employed to depress PbS, to evaluate whether a synergistic effect could occur between the two reagents for the PbS depression. Fig. 4 displays the flotation responses of PbS and $CuFeS_2$ depending on the mass ratios of H_2SO_4: starch. The initial dosage of H_2SO_4 was 600 mg/dm^3 in the tests. The PbS recovery was gradually decreased with the increase in the mass ratio of H_2SO_4 to starch. Moreover, the PbS recovery was lowered to 21.3% at a 6:1 ratio of H_2SO_4: starch. The starch concentration was 100 mg/dm^3 at the 6:1 ratio. Whereas the PbS recovery was 40.9% with 100 mg/dm^3 starch and 85.2% with 600 mg/dm^3 of H_2SO_4, The PbS recovery using the combined starch and H_2SO_4 (80 mg/dm^3 and 600 mg/dm^3) was much lower than that of each depressant at the same dosage.

Our flotation results suggest that the combination of H_2SO_4 and starch has a synergistic effect to prevent the PbS flotation. Starch tends to adsorb onto oxide surfaces, leading to the depression of oxides, such as hematite (Shrimali and Miller, 2015), cassiterite, and fluorite (Li et al., 2022; Liu et al., 2021; Zheng et al., 2024). It is possible that these oxidative species may interact with the OH groups in the starch molecule. It is expected that the H_2SO_4 treatment may increase the oxidative level of the PbS surface, assisting in the starch adsorption on the PbS surface.

3.1.2. Effects of H_2SO_4/starch reagent concentration and reaction time

The depressant dosage is crucial for the PbS flotation. For example, 2 mol/dm^3 of H_2SO_4 was required to prevent PbS flotation. Therefore, the suitable dosages of H_2SO_4 and starch were also determined by the flotation tests. The molar ratio of H_2SO_4 to starch was maintained at 6:1, and the reaction time of the mixed depressants was 6 min during these tests.

Fig. 5a illustrates the effect of H_2SO_4 dosage in the mixed depressants on the recoveries of PbS and $CuFeS_2$. As for the natural PbS sample, the recovery was below 6.7% as the H_2SO_4 dosage in the mixed depressant reached 700 mg/dm^3. In contrast, the H_2SO_4 and starch treatment did not reduce the $CuFeS_2$ recovery. As a result, the $CuFeS_2$ recovery was still 80.9%, when the $CuFeS_2$ was treated with 700 mg/dm^3 H_2SO_4 and 116.7 mg/dm^3 starch (Fig. 5a). These findings further confirm that the H_2SO_4/starch treatment does not adversely affect the floatability of $CuFeS_2$. Additionally, the optimal dosage for the combined depressant was established at 700 mg/dm^3 for H_2SO_4 and 116.7 mg/dm^3 for starch, to completely depress PbS.

The reaction time of a depressant is also a crucial factor in the PbS depression. For example, 20 min was required for H_2SO_4 to depress PbS (Xie et al., 2022). As for the H_2SO_4 (700 mg/dm^3) and starch (116.7 mg/dm^3) mixture, 3 min of reaction could highly decline the PbS recovery (33.1%). Furthermore, the PbS recovery was 6.7% by 6 min of reaction with the combined depressants (Fig. 5b). These results demonstrate that 6 min of reaction time is enough to inhibit PbS flotation with the combined depressants.

In terms of $CuFeS_2$, its recovery was 80%-90% in the entire examined reaction-time region (4-7 min), indicating again that the mixed depressant could not efficiently prevent the $CuFeS_2$ flotation.

Furthermore, the PbS recovery (9.2%) with this combined depressant was significantly lower than the recovery with 700 mg/dm^3 of H_2SO_4 (83.2%) or 116.7 mg/dm^3 of starch (32.1%). These results further highlight that a synergistic effect occurred between the two reagents for the PbS depression.

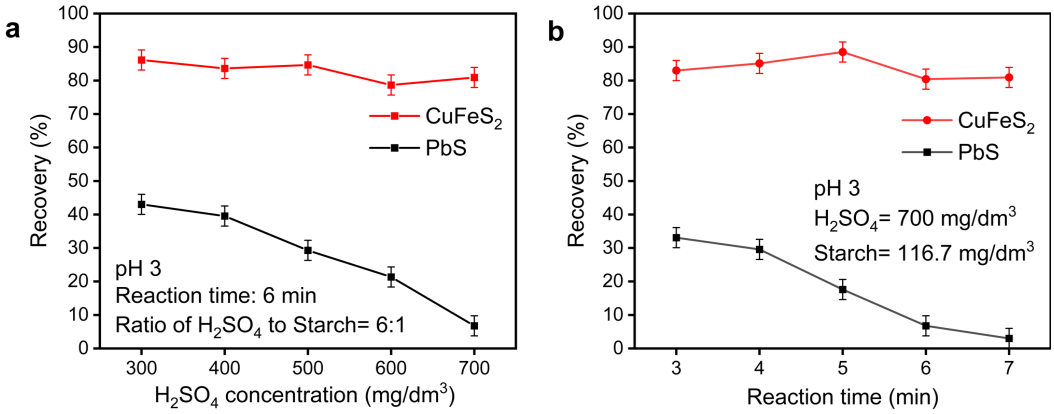

Fig. 5. Flotation recoveries of $CuFeS_2$ and PbS depending on the H_2SO_4 concentration (a) and the reaction time (b)

3.2. Hydrophobicity of mineral surfaces

Natural PbS and $CuFeS_2$ surfaces are both highly hydrophobic and thus could be floated only by a frother. To separate these two minerals, the PbS surface should be altered into a hydrophilic surface using a depressant. Here, the hydrophobicity of the minerals treated with the H_2SO_4 and starch was assessed by the contact angle tests to deeply interpret the depressing capacity of the combined depressants.

As for the natural PbS and $CuFeS_2$ surfaces, their contact angles were measured as 76.12° and 81.52°, respectively, in this work (Figs. 6 and 7). Similar results were reported in a previous work, suggesting the natural surfaces of these minerals are extremely hydrophobic (Jin et al., 2025). The H_2SO_4 and starch conditioning lowered the contact angle of the PbS surface. When the PbS was treated by the mixed depressants for 6 min, the contact angle was reduced to 38.04°. This finding demonstrates the combined treatment results in a notable decrease in the contact angle of PbS, agreeing well with our flotation results in Fig. 3. It was reported that the H_2SO_4 conditioning may induce passivation of the PbS surface, forming hydrophilic $PbSO_4$. On the other hand, since the starch molecule has multiple OH groups, this molecule shows a high level of hydrophilic. The presence of starch on the PbS surface also decreased the PbS hydrophobicity.

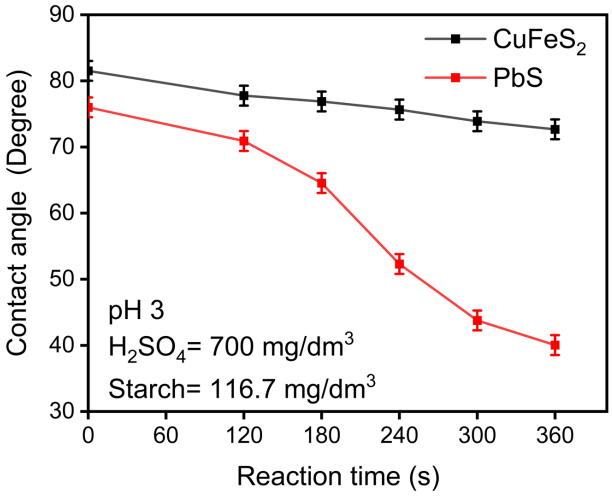

Fig. 6. Contact angle results of PbS and $CuFeS_2$ treated by H_2SO_4 and Starch at different times

Differently, the contact angle of $CuFeS_2$ exhibited no significant decrease across the reaction-time range of 0-60 min, remaining stable within 75°-80° (Figs. 6 and 7). Especially, the gap between the contact angles of PbS and $CuFeS_2$ reached 42% when the two minerals were treated by the mixed depressants for 6 min. For this reason, the combined depressants are specific depressants for PbS, which could be used for the separation of these two minerals.

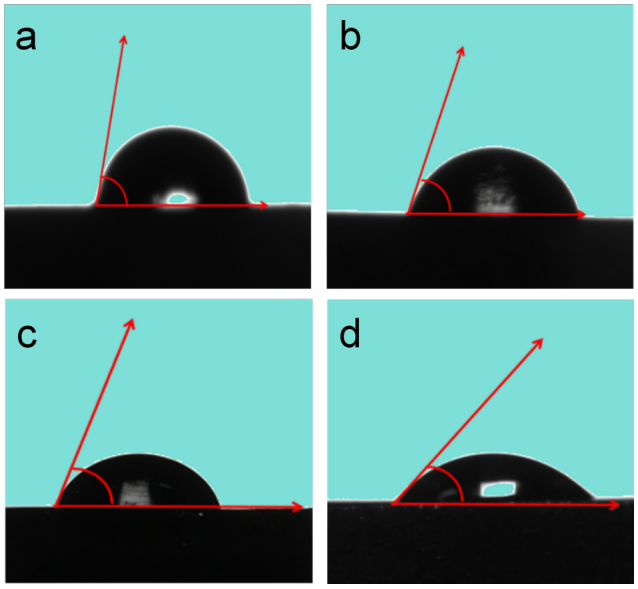

Fig. 7. Recorded photos of water droplets for the contact angle measurements: (a) original $CuFeS_2$; (b) $CuFeS_2$ conditioned with H_2SO_4/starch; (c) original PbS; (d) PbS reacted with H_2SO_4/starch (Experimental parameters are 6 min of reaction time, 700 mg/dm^3 of H_2SO_4, and 6:1 of H_2SO_4: starch ratio)

3.3. Surface component identification

3.3.1. Adsorption species on the mineral surfaces

Infrared spectroscopy is an effective means to evaluate the adsorption of organic species on mineral surfaces (Gong et al., 2024). We employed infrared spectroscopy to elucidate the interaction between the starch/ H_2SO_4 and the minerals.

Firstly, the infrared spectrum of starch was measured for comparison, Fig. 8a. Some characteristic peaks of starch were detected in the spectrum, including 2925.89 cm^{-1} for the C−H group (Warren et al., 2016), 1465.84 cm^{-1} for the $-CH_3$ group, 1168.81 cm^{-1} for the −C−O−C− group (Kar et al., 2013), and 979.80 cm^{-1} for the C−OH group (Kar et al., 2013). Moreover, as the PbS treated with H_2SO_4 and starch, the IR peak of −OH was also detected, and its position (3197.84 cm^{-1}) was similar to that (3199.78 cm^{-1}) in the starch spectrum. This suggests that starch molecules were adsorbed onto the surface of PbS. Notably, no new absorption peaks were observed in the spectrum of the PbS sample conditioned with H_2SO_4 and starch. These results reveal that the starch in the mixed depressants could physically adsorb onto the PbS surface.

Previous research indicated that the reaction between H_2SO_4 and the PbS surface may generate $PbSO_4$ components, which improve the oxidative degree of the PbS (Xie et al., 2022). However, IR peaks corresponding to the S−O bond were absent in the PbS spectrum that reacted with the combined depressant. It is plausible that the amount of $PbSO_4$ present was insufficient for detection by the IR method. Nevertheless, it is reasonable to expect that the presence of $PbSO_4$ on the PbS surface may promote the adsorption of starch because it facilitates the generation of H-bonds through interactions among the $PbSO_4$ species and starch molecules.

Fig. 8b compares the FTIR spectra of natural $CuFeS_2$ and $CuFeS_2$ treated with H_2SO_4 and starch. The characteristic peaks of starch could not be observed in the spectrum of $CuFeS_2$ reacted with the combined depressants. The $CuFeS_2$ spectrum treated by the depressants was almost the same as that of natural $CuFeS_2$. These FTIR results indicate that the treatment of H_2SO_4 and starch could not produce any new species on the $CuFeS_2$ surface.

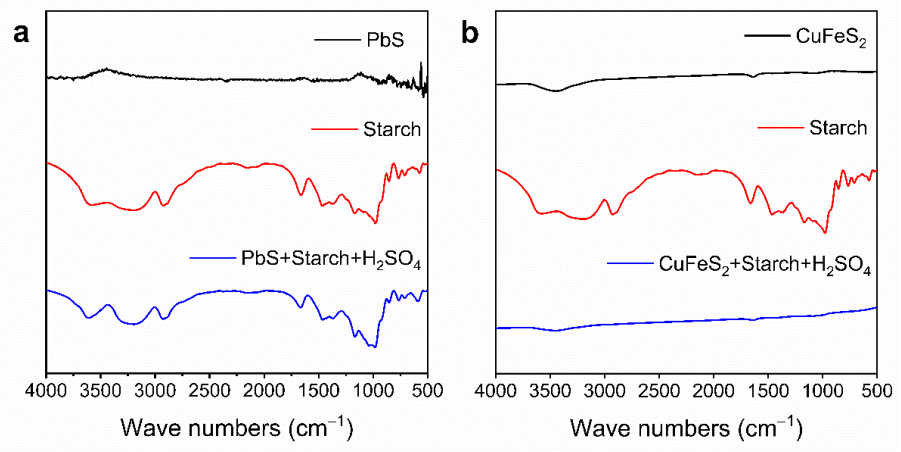

Fig. 8. FTIR spectra results of PbS (a) and $CuFeS_2$ (b) samples. Experimental parameters are: 6 min of reaction time, 6:1 of H_2SO_4: starch ratio, 700 mg/dm³ of H_2SO_4

3.3.2. Chemical states on the mineral surfaces

XPS is a prevalent tool to probe the chemical environment of an element on the mineral surface by determining the binding energy (BE) spectrum (Ghobeira et al., 2022; Yang et al., 2024). In this investigation, we utilized the XPS system to determine the variation in the components on mineral surfaces caused by the reaction with the H_2SO_4 (700 mg/dm³) and starch (116.7 mg/dm³).

In terms of the natural PbS, only two Pb (4f) peaks were observed at 137.80 and 142.66 eV in the spectrum (Fig. 9a), which are due to the Pb in PbS bulk (Cao et al., 2024b). The Pb 4f peaks of PbS bulk (137.73 eV and 142.59 eV) were also found in the spectrum of PbS reacted by the mixed depressants. A new Pb 4f doublet also occurred at 138.95 eV and 143.81 eV, which may be assigned to the PbO species (Wang et al., 2007; Wang et al., 2022). Previous work showed that 1.5 mol/dm³ of H_2SO_4 treatment generated $PbSO_4$ species that covered the PbS surface (Cao et al., 2024b). The H_2SO_4 concentration in this work was only 700 mg/dm³ (7.14×10^{-3} mol/dm³), which could not result in a full passivation of the PbS surface to generate $PbSO_4$ components.

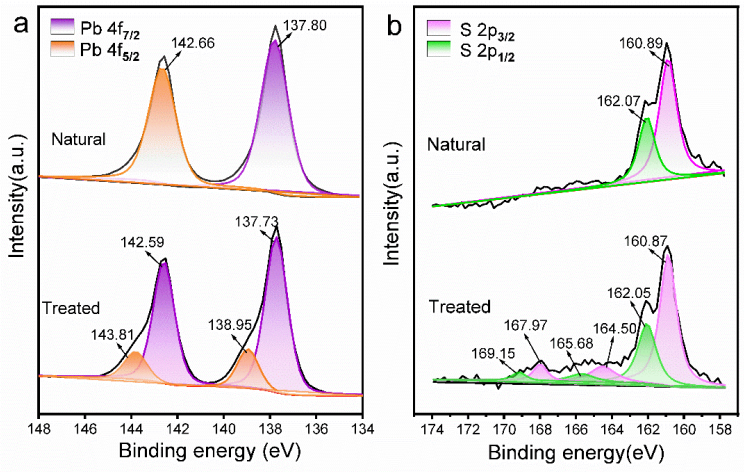

Fig. 9. XPS spectra of Pb (a) and S (b) on the natural and treated PbS (Experimental parameters are 6 min of reaction time, 700 mg/dm³ of H_2SO_4, and 116.7 mg/dm³ of H_2SO_4)

Furthermore, the percentage of PbO species among all Pb species was only 41.45%. Such a limited PbO concentration could not fully decrease the hydrophobicity of PbS. However, the above FTIR results clarify that starch was physically adsorbed on the PbS surface. The starch adsorption is the main reason for the PbS depression.

Fig. 9b displays the detailed spectra of S atoms on natural and depressed PbS surfaces. The S 2p peaks were observed at 160.89 eV and 162.07 eV in the spectrum of natural PbS, which agrees well with

the previous report (Yang et al., 2025). For PbS reacted with the mixed depressants, the peaks of S in PbS bulk were also detected at 160.87 eV and 162.05 eV. In addition, the S $2p_{3/2}$ presenting at 165.50 eV raised from the elemental S and S $2p_{3/2}$ with 167.97 eV of BE could be assigned to the SO_4^{2-} component. The H_2SO_4 treatment induces oxidation of S^{2-}species on the PbS surface (Cao et al., 2024b; Xie et al., 2021b). In this work, 700 mg/dm³ of H_2SO_4 conditioning also increased the oxidative level of the PbS surface. As a result, the concentrations of elemental S and SO_4^{2-} (in total S species) were 10.34% and 10.14%, respectively.

The XPS results of $CuFeS_2$ samples, both untreated and reacted samples using the mixed depressants, are presented in Fig. 10, to elucidate the selectivity of depressants. The BE of Cu $2p_{3/2}$ for natural $CuFeS_2$ was 932.49 eV (Fig. 10a), consistent with literature values (Khoso et al., 2019). The depressant treatment did not shift the BE of Cu in $CuFeS_2$ or generate any new Cu peaks. In the Fe XPS spectra (Fig.10b), the peak at 711.89 eV could be assigned to the Fe in the $CuFeS_2$, while the peak at 709.49 eV was caused by the FeO species (Xu et al., 2017), probably resulting from the sampling process. For the treated $CuFeS_2$, these peaks are also observed in the spectrum. While FeO concentration (8.64%) is close to that (9.03%) of the untreated sample. These findings reveal that the mixed depressants did not vary the chemical environments of Cu and Fe on the $CuFeS_2$ surface.

As for the natural $CuFeS_2$ surface, two S components were detected, i.e., S^{2-} and S_2^{2-}. The BE of S $2p_{3/2}$ of these two S species were 161.43 and 163.46 eV, Fig. 10c. The depressant treatment did not induce new S species, besides S^{2-} and S_2^{2-} species. H_2SO_4 conditioning may oxidize the $CuFeS_2$ surface, producing Cu^{2+}, Fe^{2+}, and SO_4^{2-} ions (Chen et al., 2023). These ions are then released into the solution, due to which the surface state of treated $CuFeS_2$ is comparable to that of the natural sample. Moreover, starch could not adsorb onto the $CuFeS_2$ surface to lower its hydrophobicity as indicated by our FTIR results.

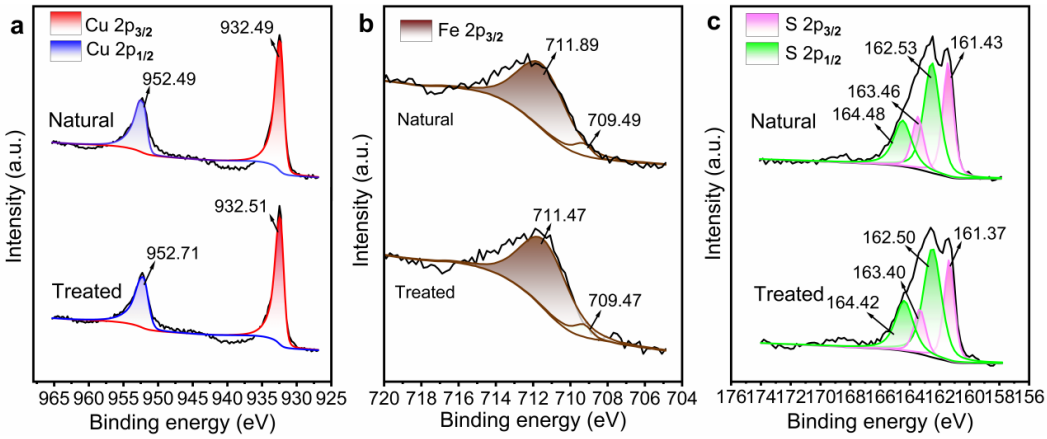

Fig. 10. XPS spectra results of Cu (a), Fe (b), and S (c) on natural $CuFeS_2$ surfaces (Experimental parameters are 6 min of reaction time, 700 mg/dm³ of H_2SO_4, and 116.7 mg/dm³ of H_2SO_4)

In this regard, XPS analysis shows that the mixed depressants treatment only improved the oxidative level of the PbS surface. As a result, Pb-O, S_0, and SO_4^{2-} were formed on the PbS surface to reduce its hydrophobicity.

3.3.3. Elemental distributions

The aforementioned XPS findings imply that the H_2SO_4/starch conditioning generated oxidative components on the PbS surface. Here, the SEM-EDS technique was used to examine the variations in elemental concentrations on the mineral surfaces, to reveal the difference in oxidation levels between PbS and $CuFeS_2$ surfaces. This approach successfully evaluates the amount of oxidative species on the PbS surface (Cao et al., 2024c; Zhang et al., 2024).

Fig. 11 presents the distribution maps of elements across the natural and treated PbS surfaces (700 mg/dm³ H_2SO_4 and 116.7 mg/dm³ starch). Elements of Pb and S were uniformly distributed in the whole examined area of the original PbS surface, while 1.60% of O was also measured in this work (Fig. 12a), potentially resulting from the oxidation of PbS in the sampling process. Whereas, as the PbS was

conditioned with the combined depressants solution, the concentration of O was increased to 10.37%. Meanwhile, Pb and S concentrations were decreased to 82.29% and 7.34%, respectively. There are two sources for the increase of O atoms on the PbS surface. First, the H_2SO_4 conditioning produced SO_4^{2-} and Pb-O species, which gave a rise in the O concentration. Secondly, the starch molecule has a large amount of OH groups, and the adsorption of this molecule could raise the O concentration. In this regard, the H_2SO_4 and starch combination could improve the hydrophilic state of the PbS surface efficiently.

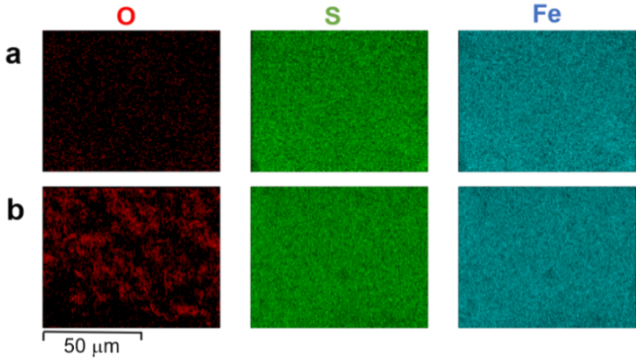

Fig. 11. SEM image of elemental distribution on PbS surfaces: (a) natural PbS; (b) PbS reacted with H_2SO_4 (700 mg/dm³) and Starch (116.7 mg/dm³)

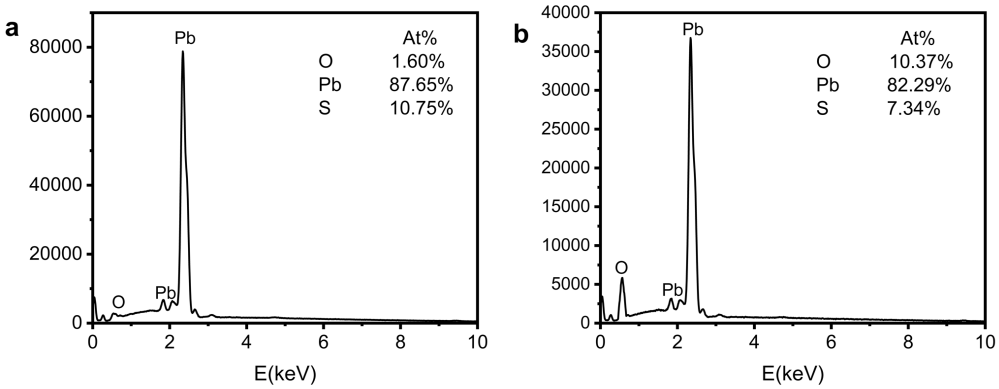

Fig. 12. EDS spectra of natural PbS (a) and PbS (b) with H_2SO_4 (700 mg/dm³) and Starch (116.7 mg/dm³)

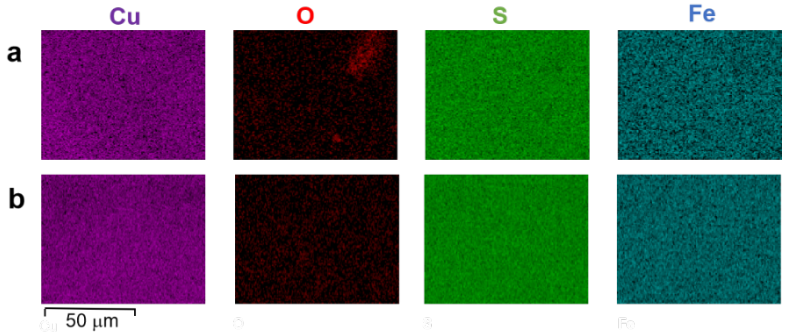

Fig. 13. SEM image of elemental distribution on $CuFeS_2$ surface: (a) natural $CuFeS_2$; (b) $CuFeS_2$ treated by H_2SO_4 (700 mg/dm³) and Starch (116.7 mg/dm³)

The elemental distribution images of the $CuFeS_2$ surfaces are plotted in Fig. 13. In the case of the natural $CuFeS_2$ surface, the O percentage was only 1.41%, which may be due to the oxidation of the sample. As the $CuFeS_2$ reacted with the mixed depressants (Fig. 14b), the variation in concentration of each element was less than 5%, compared to the results of the natural sample. Moreover, the O concentration was only 1.17%, which was similar to that of the natural sample (Fig. 14a). This indicates

that the H_2SO_4/starch system had a negligible influence on the elemental ratios of the $CuFeS_2$ surface. Overall, these EDS findings confirm that the mixed depressants primarily reacted with the PbS surface instead of the $CuFeS_2$ surface. This result is consistent with the above XPS results.

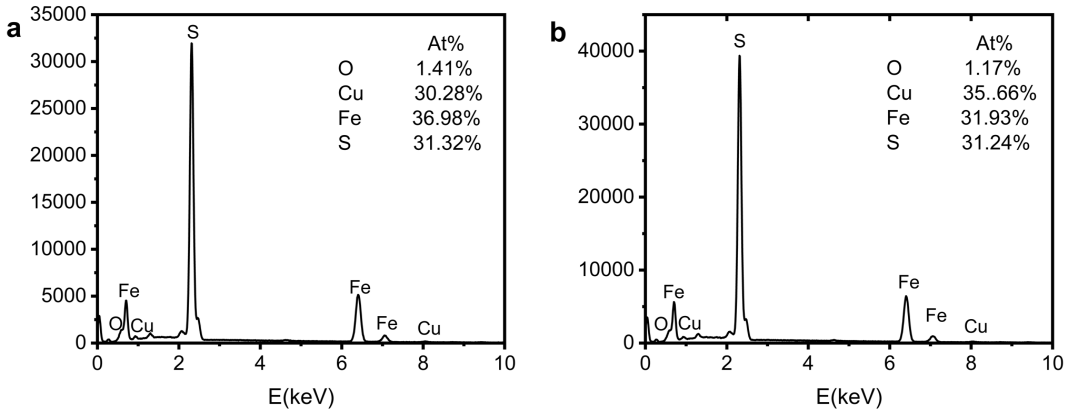

Fig. 14. Distribution of $CuFeS_2$ surface elements with/without H_2SO_4 (700 mg/dm^3) and Starch (116.7 mg/dm^3)

According to the results from the above FTIR, XPS, and SEM experiments, a model regarding the interaction between the depressants and PbS was reported in Fig. 14: The PbS surface may be oxidized in the H_2SO_4 solution. Consequently, oxidative species, including Pb-O (major species) and SO_4^{2-}, were produced on the PbS surface. These O-bearing components may interact with the OH group in the starch molecules to generate H-bonds, which enhance the adsorption of starch molecules. These starch molecules may cover the PbS surface to efficiently lower its hydrophobicity, which prevents PbS particles from adhering to air bubbles. In contrast, the treatment of mixed depressants does not vary the components of the $CuFeS_2$ surface. Moreover, starch molecules did not adsorb onto the $CuFeS_2$ surface either. In this regard, the $CuFeS_2$ surface maintains its hydrophobicity, and $CuFeS_2$ particles can be captured by air bubbles.

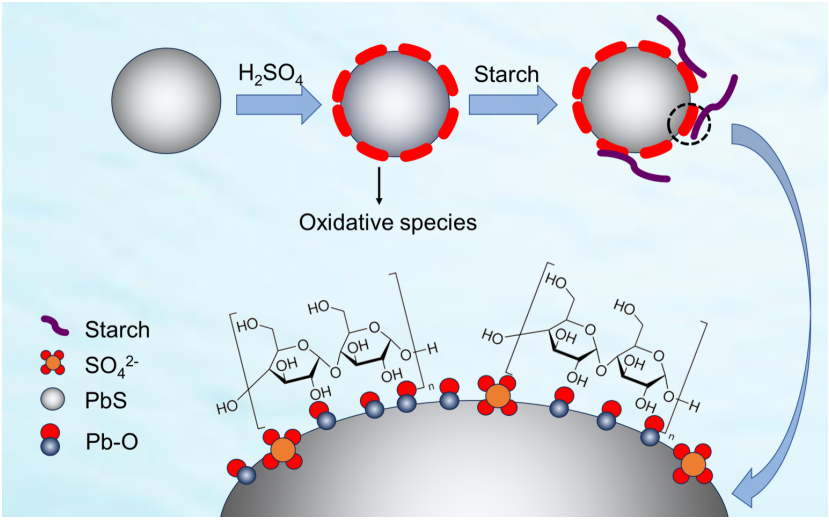

Fig. 15. Starch adsorption mechanism diagram

4. Conclusions

(1) The combination of H_2SO_4 and starch exhibits a synergistic effect on the depression of galena, thereby reducing the dosage of depressants. The recovery of PbS was only 6.7% using 700 mg/dm^3 H_2SO_4 and 116.7 mg/dm^3 starch.

(2) When PbS was treated with the mixture of H_2SO_4 and starch, the interaction between H_2SO_4 and the PbS surface produced oxidative components, i.e., Pb-O and SO_4^{2-}. These oxidative species may

interact with the OH groups in starch molecules to generate H-bonds, enhancing the adsorption of starch molecules and thus efficiently producing a hydrophilic PbS surface.

(3) In contrast, the interaction of H_2SO_4 with the $CuFeS_2$ surface did not produce new oxidation components. Furthermore, starch could not absorb onto the $CuFeS_2$ surface either. Consequently, the $CuFeS_2$ floatability remained largely unchanged after the treatment with the mixed depressants. Therefore, $CuFeS_2$ can still be effectively floated by air bubbles and separated from PbS.

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