

Article

Selective Oxidation Depression of Copper-Activated Sphalerite by H₂O₂ During Chalcopyrite Flotation

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Abstract

Using hydrogen peroxide (H₂O₂), a simple and easily accessible reagent, as a selective depressant, flotation separation experiments of chalcopyrite and copper-activated sphalerite were conducted. The micro-flotation tests of single minerals indicated that H₂O₂ selectively depresses copper-activated sphalerite and exerted almost no depressant effect on chalcopyrite. In the flotation tests of artificially mixed minerals, a copper concentrate with a grade of 29.95% and a recovery of 87.30% was obtained, while the zinc content was only 5.76%, demonstrating a significant separation effect. The results of contact angle measurement, Zeta potential measurement, surface adsorption analysis, and XPS analysis suggested that H₂O₂ had a stronger oxidation capacity on the surface of copper-activated sphalerite than chalcopyrite, generating hydrophilic hydroxyl groups on the surface of sphalerite and preventing further adsorption of the collector Z-200 on the surface of sphalerite.

Keywords: chalcopyrite; copper-activated sphalerite; flotation separation; H₂O₂; oxidation depression



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1. Introduction

Chalcopyrite and sphalerite commonly occur as intergrown or finely disseminated phases within massive sulfide ores and are often associated with other sulfide minerals such as pyrite and galena [1–3]. Flotation is the most mature technique for separating Cu–Zn mixed sulfide ores. Because chalcopyrite floats more readily than sphalerite, the usual approach is to float chalcopyrite while depressing sphalerite. In the past, inorganic depressants such as sodium sulfite, zinc sulfate, or sulfate-based mixtures were commonly used, with lime serving as the pH modifier. Under strong alkaline conditions, zinc sulfate can precipitate as hydrophilic zinc hydroxide on the surface of sphalerite, thereby depressing its flotation [4,5]. However, in an alkaline flotation system, tightly intergrown Cu–Zn sulfides form a galvanic cell: chalcopyrite preferentially releases Cu²⁺, which deposits onto the sphalerite surface to form a copper-activated coating [6]. This greatly enhances the adsorption of collectors (e.g., xanthates or sodium diethyldithiocarbamate) on sphalerite, causing the activated sphalerite to float alongside chalcopyrite. As a result, copper and zinc become mutually entrained in the copper concentrate, making it difficult to produce high-grade copper and zinc concentrates.

In response to the above issues, researchers have therefore turned to environmentally friendly organic depressants such as starches, polysaccharides, and synthetic polymers [7–9]. However, most organic depressants exhibit weak adsorption and poor selectivity toward copper-activated sphalerite. For example, when using high-molecular-weight agents like sodium polyacrylate or carboxymethyl cellulose, sphalerite is only depressed at high dosages, at which point chalcopyrite is also adversely affected [10,11]. Likewise, macromolecular organics such as chitosan derivatives have shown some depression in laboratory tests, but their high cost and inconsistent performance make large-scale industrial application impractical [12,13]. In addition, some researchers have found that different sulfide minerals exhibit varying degrees of susceptibility to oxidation. Commonly used oxidizing agents include oxygen, hydrogen peroxide, hypochlorous acid, and potassium permanganate. An appropriate level of oxidation can enhance the flotation recovery of chalcopyrite, whereas oxidation tends to reduce the floatability of minerals such as sphalerite and pyrite by forming stable, hydrophilic surface coatings of metal oxides or hydroxides [14–16]. However, in the context of chalcopyrite–sphalerite separation, the differences in oxidation behavior and the underlying mechanisms between these two minerals remain unclear.

In this study, it was found that under near-neutral pH conditions, the addition of low concentrations of H_2O_2 to the flotation pulp oxidatively depress copper-activated sphalerite selectively, while exerting negligible depressive effects on chalcopyrite. Through single-mineral micro-flotation tests, contact angle measurements, zeta potential analysis, surface adsorption analysis, solution chemistry calculations, and X-ray photoelectron spectroscopy (XPS) characterization, the mechanism by which H_2O_2 operates in Cu–Zn flotation separation was elucidated. These results demonstrate that H_2O_2 is a viable depressant that effectively addresses the long-standing issue of copper-activated sphalerite in chalcopyrite flotation [17–20]. Moreover, this approach offers a novel pathway for developing more sustainable and economical Cu–Zn separation processes in sulfide mineral processing.

2. Materials and Methods

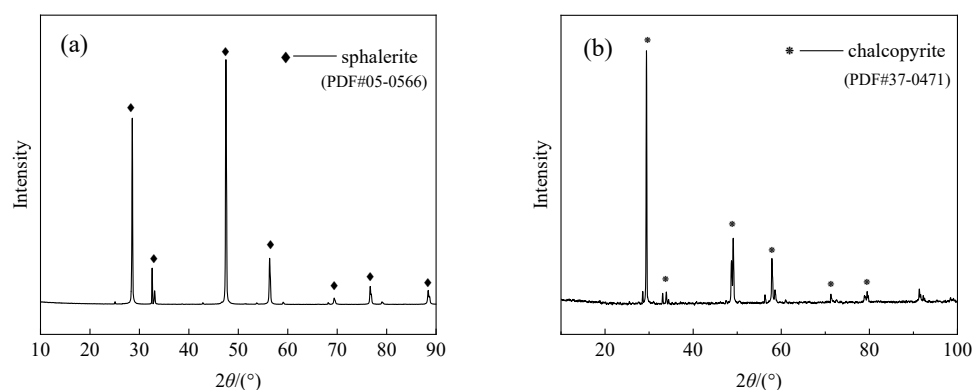
2.1. Materials

The pure mineral samples of chalcopyrite and sphalerite used in this study were obtained from Wenshan Prefecture, Yunnan Province, China. Firstly, the raw ores with good crystallization were manually selected to remove gangue and other impurities, obtaining high-purity samples. Then, the selected samples were ground finely in a ceramic ball mill and sieved dryly with a standard sieve. The mineral particles with a size of 38–74 μm were collected and stored in vacuum bags as samples for micro-flotation experiments. The samples with a size of <38 μm were further ground to <2 μm in an agate mortar for Zeta potential measurement, chemical multi-element analysis, and X-ray diffraction (XRD, Shimadzu XRD-7000S, Kyoto, Japan) analysis.

Table 1 presents the chemical analysis results of the samples. It can be seen from Table 1 that the Cu content of chalcopyrite is 34.32% and the Zn content of sphalerite is 64.01%, indicating that the purity of both chalcopyrite and sphalerite is above 95%. Figure 1 shows the XRD patterns of the analyzed mineral samples. As shown in the figure, the purity of both minerals is very high, with almost no other impurities, meeting the requirements for pure mineral experiments.

Table 1. Results of chemical compositions analysis of sphalerite and chalcopyrite.

Sample \ Content/wt. %	Zn	Cu	Fe	S	Pb	Si
Sphalerite	64.01	<0.005	1.49	33.75	0.031	0.34
Chalcopyrite	0.024	34.32	30.32	34.12	0.068	0.27

**Figure 1.** XRD pattern of sphalerite (a) and chalcopyrite (b).

During the experiment, the collector used was sodium ethyl xanthate (Z-200), the frother was terpeneol oil, the depressant was H_2O_2 , and the activator was copper sulfate ($CuSO_4$). The pulp pH was maintained at natural neutrality, and all experiments were conducted using deionized water. Specifically, Z-200 (≥ 95.0 wt.% purity) and 3.0 wt.% H_2O_2 in aqueous solution were both purchased from Macklin Biochemical Technology Co., Ltd. (Shanghai, China); terpeneol oil (analytical grade) was obtained from Xilong Chemical Co., Ltd. (Chengdu, China); and $CuSO_4$ (analytical grade) was supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Micro-Flotation Experiments

All micro-flotation experiments were conducted using an XFG-series laboratory flotation machine (Jitan Machinery Co., Ltd., Jinan, China) with a cell volume of 60 mL and a fixed impeller speed of 1600 rpm. The micro-flotation workflow (Figure 2) began by ultrasonically pre-treating 2.0 g of sample for 2 min to remove the mineral's surface oxide layer. After sonication, the sample was transferred into the flotation cell, 50 mL of deionized water was added, and the machine was started. Activator ($CuSO_4$, 0.3 wt.%), oxidant/depressant (H_2O_2 , 3.0 wt.%), collector (Z-200, ≥ 95.0 wt.%), and frother (terpeneol oil, ≥ 65.0 wt.%) were subsequently introduced into the pulp, with corresponding conditioning times of 2 min, 2 min, 3 min, and 1 min, respectively. Flotation was then conducted with air inflation and froth scraping for 4 min. Finally, the concentrate (froth product) and tailings (cell product) were separately filtered, dried, and weighed; recovery was calculated using Equation (1). Grade is determined through multi-element chemical analysis. Each experiment was repeated three times.

$$\varepsilon = \frac{m1}{m1 + m2} \times 100\% \quad (1)$$

where ε represents flotation recovery (%); $m1$ represents the mass (g) of the concentrate; $m2$ represents the mass (g) of tailings.

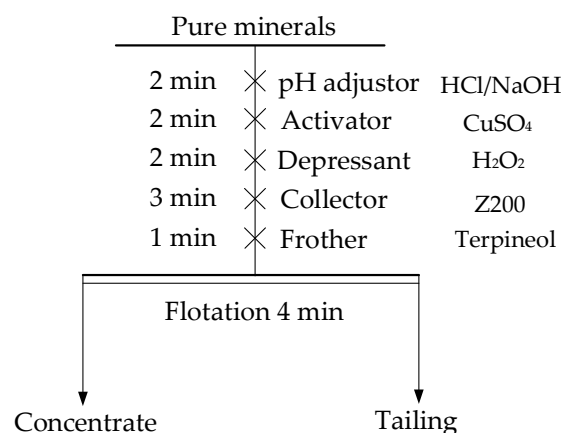


Figure 2. Flowsheet of micro-flotation experiments.

Definition of terms: Grade refers to the mass fraction of a specific valuable element or mineral in the concentrate, tailings, or raw ore. Recovery refers to the ratio of the total amount of a valuable component recovered from the raw ore during the beneficiation process to the total amount of that component originally present in the raw ore.

2.3. Contact Angle Measurements

In order to evaluate changes in surface wettability before and after reagent treatment, contact angle measurements were performed on chalcopyrite and sphalerite surfaces. The mineral specimens used were high-purity, single-mineral samples, and measurements were conducted on a JY-82C automated video contact angle goniometer (Dingsheng Tester, Dingsheng Group, Yangzhong, China) using the sessile drop method. Rectangular blocks of approximately $1.0\text{ cm} \times 1.0\text{ cm} \times 0.5\text{ cm}$ were cut and sequentially polished from coarse to fine using TOA-brand abrasive paper until the surfaces were smooth and flat. The polished samples were then rinsed with deionized water followed by absolute ethanol and dried under a stream of high-purity nitrogen gas. Reagent conditioning was performed in flotation order: each sample was placed in a beaker containing 50 mL of deionized water, after which activator (CuSO_4), depressant (H_2O_2), and collector (Z-200) were added sequentially and stirred for 10 min to ensure a thorough interaction with the mineral surface. Following reagent treatment, each sample was removed, rinsed three times with deionized water to eliminate unadsorbed reagents, and then blown dry under high-purity nitrogen. Finally, a 3–5 μL droplet of deionized water was placed on the mineral surface, and once the droplet stabilized, the contact angle was automatically recorded via video imaging. Each experiment was repeated three times.

2.4. Zeta Potential Measurements

Zeta potential refers to the electric potential at the shear plane of the electric double layer formed around mineral particles in a liquid medium. It reflects the charge interactions between the mineral surface and the surrounding liquid, serving as an indirect indicator of the surface charge characteristics of the particles. To assess how flotation reagents affect surface charge, the Zeta potential of chalcopyrite and Cu-activated sphalerite was measured under different treatments. A Malvern Zetasizer Nano (Malvern Panalytical, Almelo, The Netherlands) was used, with $1 \times 10^{-3}\text{ mol/L}$ KCl as the background electrolyte. For each test, 0.02 g of mineral (particle size $< 2\text{ }\mu\text{m}$) was mixed into 50 mL of KCl solution and stirred for 1 min. The pH was then adjusted to the target value using 0.1 mol/L NaOH or HCl and stirred for another 2 min. Reagents were added in flotation order— CuSO_4 , H_2O_2 , and Z-200—each followed by 2 min of stirring. After conditioning, the slurry was

left undisturbed for 10 min to allow coarse particles to settle, and the clear supernatant was withdrawn for Zeta potential measurement. Each experiment was repeated three times.

2.5. Surface Adsorption Measurements

To compare reagent adsorption on the mineral surface under different conditions, the total organic carbon (TOC) concentration of the post-reaction solution was measured using a Vario TOC analyzer (Elementar, Langenselbold, Germany). In each test, 50 mL of deionized water and 2.0 g of the mineral sample were placed in the flotation cell, the pH was adjusted to the preset value, and then the pH modifier and collector (Z-200) were added sequentially, with the slurry stirred for 10 min to ensure complete interaction. After conditioning, the supernatant was filtered and retained for TOC analysis. The amount of collector adsorbed on each mineral surface (mg/g) was calculated according to Equation (2) by comparing initial and residual TOC concentrations.

$$\Gamma = \frac{(C_0 - C_1)V}{CM} \quad (2)$$

Here, Γ is the reagent adsorption amount (mg/g);

C_0 and C_1 are the initial and post-adsorption TOC values (mg/L), respectively;

V is the solution volume (L);

C is the reagent's carbon content percentage;

M is the mineral sample mass (g).

2.6. XPS Measurements

In each experiment, 2 g of the mineral sample was placed in a beaker and an appropriate amount of deionized water was added. The sample was then subjected to ultrasonic cleaning for 2 min to remove surface oxides. After cleaning, the sample was conditioned in the following order: activator (CuSO_4), depressant (H_2O_2), and collector (Z-200), then filtered and dried in a vacuum oven at 35 °C. Finally, the dried sample was analyzed using a Thermo Scientific Nexsa XPS system (Thermo Fisher Scientific, Waltham, MA, USA) with Al K α excitation (1486.6 eV). All binding energies were calibrated to the C–C reference peak at 284.8 eV to compensate for the surface-charging effects.

3. Results and Discussion

3.1. Single-Mineral Flotation Results

As shown in Figure 3a, under the flotation conditions of pH 7, 10 mg/L Z-200 as collector, 1.5×10^{-5} mol/L CuSO_4 as activator for sphalerite, and 8 mg/L terpeneol as frother, the flotation recovery of Cu-activated sphalerite decreases significantly with increasing H_2O_2 dosage, while chalcopyrite recovery remains nearly unaffected when H_2O_2 is below 8 mmol/L. Specifically, both minerals exhibit good floatability at low H_2O_2 concentrations; however, as the H_2O_2 dosage increases, the recovery of activated sphalerite drops sharply—from 90.06% to 14.42% at 8 mmol/L—whereas chalcopyrite recovery decreases by only 1.07%, remaining at a high level. Under these conditions, effective separation between chalcopyrite and Cu-activated sphalerite can be achieved.

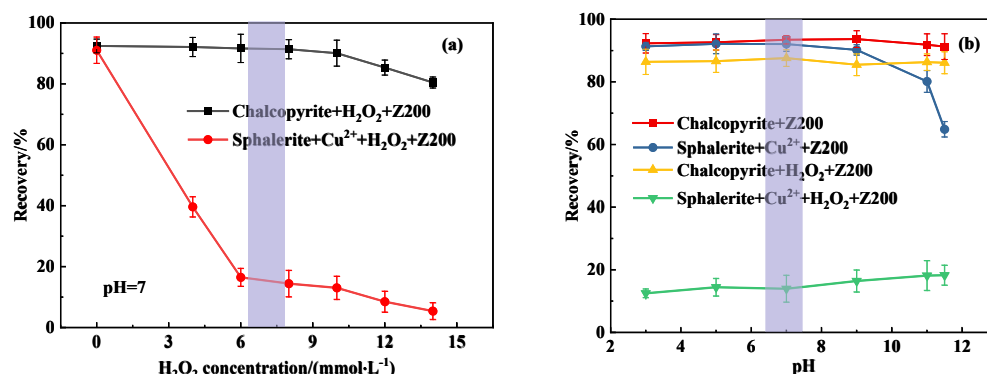


Figure 3. Effect of different depressant dosage (a) and pH (b) on chalcopyrite and sphalerite surfaces: Both (a,b) are single-mineral flotation.

Figure 3b further illustrates the recovery of individual minerals under varying pH conditions with Z-200 (10 mg/L), both alone and with the addition of H_2O_2 (8 mmol/L) + Z-200 (10 mg/L). Cu-activated sphalerite shows strong suppression under mildly acidic-to-neutral conditions in the presence of H_2O_2 , resulting in low recovery. This suppression weakens at higher pH, likely due to the decreased stability of H_2O_2 in alkaline media, where it readily decomposes into O_2 and H_2O , reducing its oxidative inhibition capacity. In contrast, chalcopyrite maintains high recovery across the entire pH range, with only a modest decrease (~5%) upon H_2O_2 addition, indicating minimal impact.

These results suggest that H_2O_2 selectively suppresses Cu-activated sphalerite with minimal effect on chalcopyrite. This is likely because H_2O_2 , as a strong oxidant, preferentially oxidizes copper and zinc sulfide species on the sphalerite surface. The resulting hydrophilic oxidation products, such as $Zn(OH)_2$ and $Cu(OH)_2$, form surface films that hinder collector adsorption and depress flotation [21]. In comparison, H_2O_2 has limited influence on chalcopyrite, possibly due to the inability to form stable hydrophilic films on its surface at low-to-moderate dosages. However, at higher H_2O_2 concentrations, chalcopyrite recovery also begins to decline, indicating a threshold beyond which oxidative effects become significant [22].

3.2. Flotation Results of Artificially Mixed Minerals

To verify the selective depression effect of H_2O_2 , chalcopyrite and Cu-activated sphalerite were mixed in a 1:1 mass ratio. Under neutral conditions (pH 7) with 10 mg/L Z-200, 8 mmol/L H_2O_2 , and 1.5×10^{-5} mol/L $CuSO_4$, the flotation separation of the two minerals was investigated, as shown in Figure 4 and Table 2. Without H_2O_2 , Cu^{2+} activation renders Z-200 equally effective on both sulfide minerals, yielding an elevated flotation product recovery of 94.99% and making separation difficult. After adding H_2O_2 , the Cu grade in the copper concentrate increased from 16.17 wt.% to 29.95 wt.% (recovery = 87.30%), while the Zn grade dropped from 29.54 wt.% to 5.76 wt.%. Conversely, the zinc concentrate reached 54.12 wt.% Zn with a 91.02% recovery. These results demonstrate that H_2O_2 enables effective separation of Cu-activated sphalerite from chalcopyrite in mixed ores, showing strong practical applicability for industrial flotation.

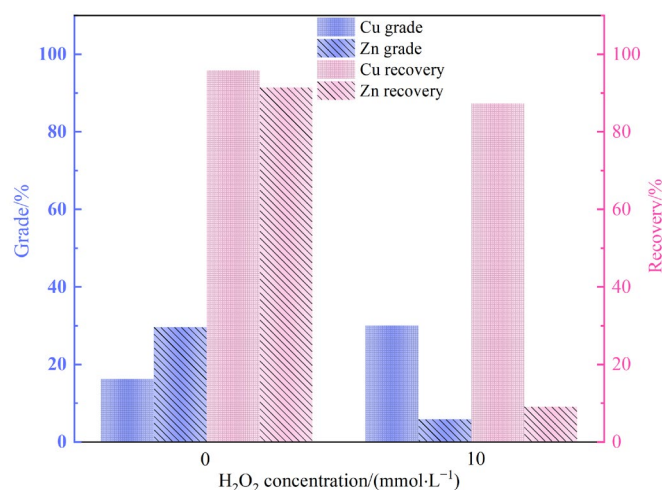


Figure 4. Flotation results of artificially mixed minerals of chalcopyrite and copper-activated sphalerite (pH = 7, H₂O₂ dosage 8 mmol/L).

Table 2. Results of flotation separation of artificially mixed minerals.

Concentration of Depressant H ₂ O ₂ /(mmol·L ⁻¹)	Product	Yield/wt. %	Grade/%		Recovery/%	
			Cu	Zn	Cu	Zn
0	Cu concentrate	94.99	16.17	29.54	95.84	91.46
	Zn concentrate	5.01	13.31	52.33	4.16	8.54
	Feed	100.00	16.03	30.68	100.00	100.00
8	Cu concentrate	48.11	29.95	5.76	87.30	8.98
	Zn concentrate	51.89	4.04	54.12	12.70	91.02
	Feed	100.00	16.51	30.85	100.00	100.00

3.3. Contact Angle Test Results

According to flotation principles, mineral floatability is governed by surface hydrophobicity, which is typically evaluated by contact angle measurements—higher contact angles indicate greater hydrophobicity and improved floatability [23–25]. Therefore, contact angles of chalcopyrite and Cu-activated sphalerite were measured under three conditions: without reagents, with Z-200, and with combined Z-200 and H₂O₂ treatment, as shown in Figure 5.

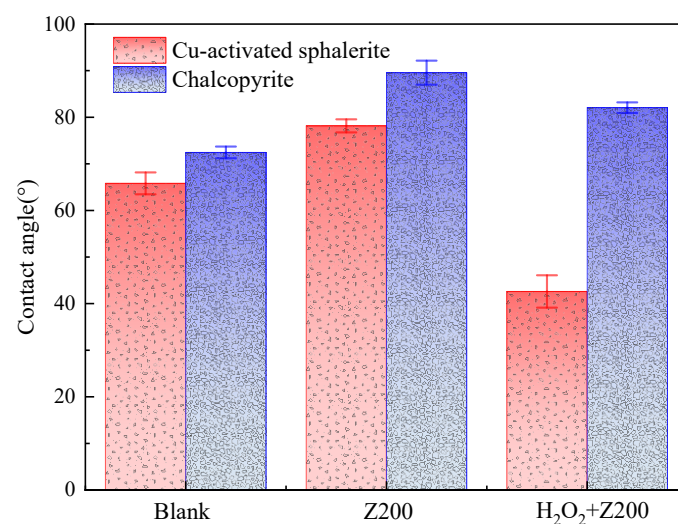


Figure 5. Surface contact angles of chalcopyrite and Cu-activated sphalerite.

Under reagent-free conditions, the contact angles of Cu-activated sphalerite and chalcopyrite were approximately 66.54° and 71.52° , respectively, indicating good inherent hydrophobicity. Upon addition of the collector Z-200, the contact angles increased significantly to 77.51° for Cu-activated sphalerite and 90.07° for chalcopyrite, suggesting effective adsorption of Z-200 and enhanced hydrophobicity for both minerals. However, with the combined application of Z-200 and H_2O_2 , the minerals exhibited distinct differences in surface wettability. The contact angle of Cu-activated sphalerite dropped sharply to 43.56° , indicating a substantial reduction in hydrophobicity, likely due to oxidative reactions with H_2O_2 forming hydrophilic hydroxyl species on the surface. In contrast, chalcopyrite maintained a contact angle of 82.13° , suggesting minimal surface alteration by H_2O_2 . This selective change in wettability provides the basis for effective flotation separation of chalcopyrite from Cu-activated sphalerite in mixed mineral systems.

3.4. Zeta Potential Test Results

As shown in Figure 6a, as pH increases from 4 to 11, the zeta potential of sphalerite decreases gradually from approximately -7 mV to -22 mV. Cu-activated sphalerite exhibits overall more negative zeta potentials (roughly -10 mV to -23 mV) compared with unactivated sphalerite. Adsorbed Cu^{2+} on the sphalerite surface likely forms copper sulfide or hydroxide complexes, rendering the surface more negative and more hydrophobic, which favors subsequent collector adsorption [4]. After adding Z-200, the zeta potential of Cu-activated sphalerite experiences a slightly positive shift, possibly because the Cu–thionocarbamate complex is overall electrically neutral or slightly positive, forming a passive layer that partially neutralizes surface negative charge. Upon addition of H_2O_2 , surface oxidation produces oxides or hydroxides (e.g., Zn-OH , Cu-OH), as well as possibly strongly negative sulfur–oxygen species (such as surface SO_4^{2-} or ZnSO_4), causing further negative shifts in zeta potential [26].

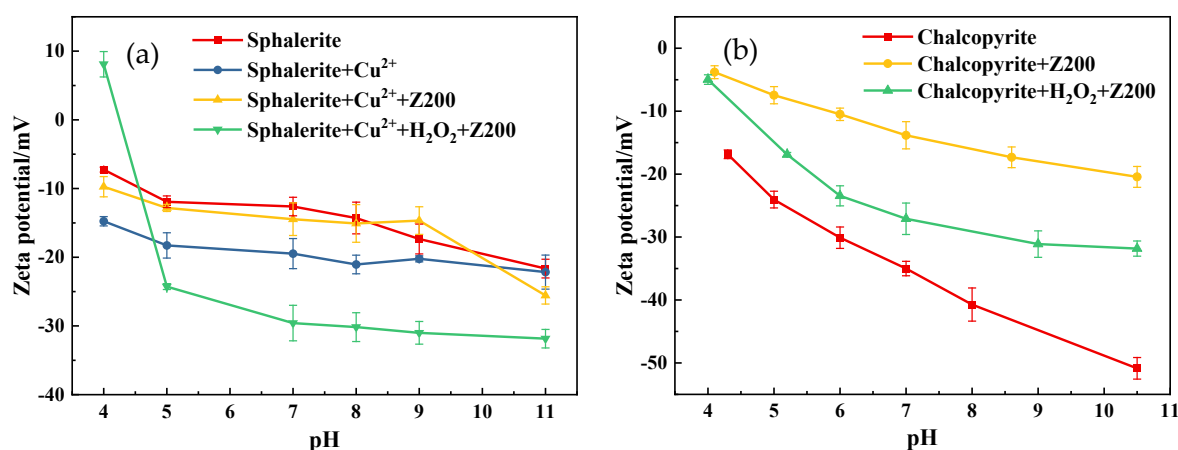


Figure 6. Zeta potential of chalcopyrite (a) and sphalerite (b) as function of pH before and after treatment with flotation reagents.

In Figure 6b, chalcopyrite's zeta potential decreases from about -17 mV at pH 4.3 to -50 mV at pH 10.5 [27]. At all pH values, chalcopyrite's zeta potential is more negative than that of sphalerite, primarily because its surface $\text{Fe}^{2+}/\text{Cu}^+$ hydrolysis is stronger, yielding more negatively charged oxide or hydroxide species [28,29]. After adding Z-200, its adsorption on chalcopyrite is stronger than on sphalerite, forming a more stable adsorption layer and producing a larger positive shift in zeta potential. With H_2O_2 +Z-200 treatment, H_2O_2 also oxidizes chalcopyrite to form metal hydroxides, shifting its zeta potential negatively. However, because sphalerite is more easily oxidized and its

oxidation products carry stronger negative charge, the negative shift in zeta potential is less pronounced than for sphalerite [30,31]. Moreover, it has been reported that the effect of zeta potential variation on flotation performance is less significant than that of contact angle, which more directly reflects the surface hydrophobicity of minerals [32].

3.5. Surface Adsorption Analysis

Table 3 shows that without H_2O_2 , Z-200 adsorbed 0.0911 mg/g on chalcopyrite and 0.0528 mg/g on Cu-activated sphalerite, indicating strong adsorption on both minerals but greater affinity for chalcopyrite. After adding H_2O_2 , Z-200's adsorption on Cu-activated sphalerite dropped to 0.0144 mg/g (a 72.7% decrease), demonstrating that H_2O_2 strongly inhibits collector adsorption on Cu-activated sphalerite. In contrast, chalcopyrite's adsorption decreased to 0.0767 mg/g (about a 16% decrease), indicating only a minor effect of H_2O_2 on its collector uptake. These results explain the large difference in floatability after H_2O_2 addition, enabling effective flotation separation of the two minerals, consistent with the flotation data [33,34].

Table 3. Results of surface adsorption.

Test Condition	C_0/mg	C_1/mg	V/L	C/%	M/g	Γ (mg/g)
Sphalerite+ Cu^{2+} +Z-200	2.90	1.80				0.0528
Sphalerite+ Cu^{2+} + H_2O_2 +Z-200	2.80	2.50	0.05	52.13%	2	0.0144
Chalcopyrite+Z-200	2.90	1.00				0.0911
Chalcopyrite+ H_2O_2 +Z-200	2.80	1.20				0.0767

3.6. XPS Analysis

XPS analyses were performed on Cu-activated sphalerite before and after interaction with Z-200 and with Z-200+ H_2O_2 to elucidate the mechanisms of Z-200 and H_2O_2 on the mineral surface. In X-ray photoelectron spectroscopy (XPS) analysis, the C 1s, O 1s, Zn 2p, and S 2p orbitals, which exhibit strong signals and high sensitivity, are selected as representative peaks for C, O, Zn, and S, respectively. This facilitates the acquisition of clear spectral peaks and enables reliable quantitative analysis [35]. The results are shown in Figure 7 and Table 4.

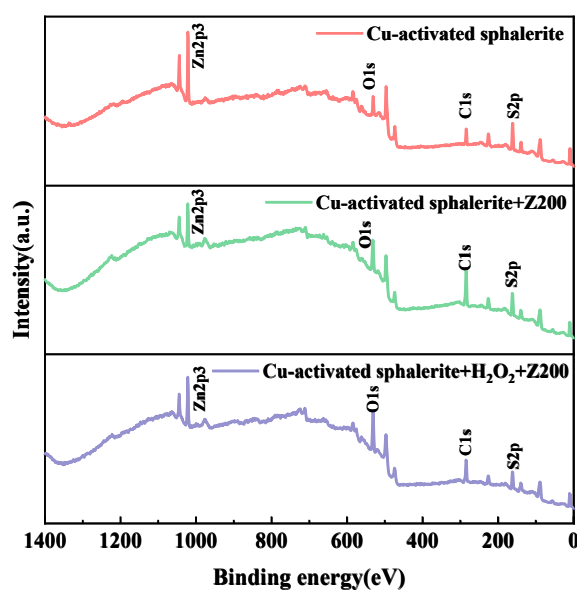


Figure 7. XPS scanning of Cu-activated sphalerite surfaces before and after reaction with Z-200 and mixtures of Z-200 and H_2O_2 .

Table 4. Atomic concentration of Cu-activated sphalerite surface before and after reaction with Z-200 and mixtures of Z-200 and H₂O₂ from XPS high-resolution spectra.

Samples	At. %			
	C1s	O1s	Zn2p	S2p
Cu-activated sphalerite	39.60	20.41	20.67	19.32
Cu-activated sphalerite+Z-200	56.66	26.02	5.47	11.84
Cu-activated sphalerite+H ₂ O ₂ +Z-200	43.24	34.45	11.90	10.41

On the untreated Cu-activated sphalerite surface, the atomic concentrations of C, O, Zn, and S were 39.60%, 20.41%, 20.67%, and 19.32%, respectively. After adding Z-200, the C content increased from 39.60 at. % to 56.66 at. %, indicating adsorption of the carbon-rich Z-200 on the mineral surface. The O content also rose, likely due to oxygen in the adsorbed Z-200. Concurrently, Zn and S concentrations decreased markedly, suggesting that Z-200 chemically interacted with surface Zn and S, masking these elements. When both H₂O₂ and Z-200 were applied, the C content dropped to 40.41%, demonstrating that H₂O₂ inhibited Z-200 adsorption. In contrast, O increased sharply to 34.45%, showing that H₂O₂'s strong oxidation enhanced surface oxidation, which is detrimental to collector adsorption. Compared to untreated sphalerite, Zn and S contents decreased by 8.77% and 8.91%, respectively, implying that H₂O₂ corroded and dissolved the sphalerite surface, forming oxygen-containing metal oxides.

To more clearly present changes in elemental concentrations and chemical environments before and after interaction with Z-200 and Z-200 +H₂O₂, the fractional peak fitting and content changes in O1s, Zn 2p, and S 2p under different conditions were analyzed, as shown in Figure 8 and Tables 5–7.

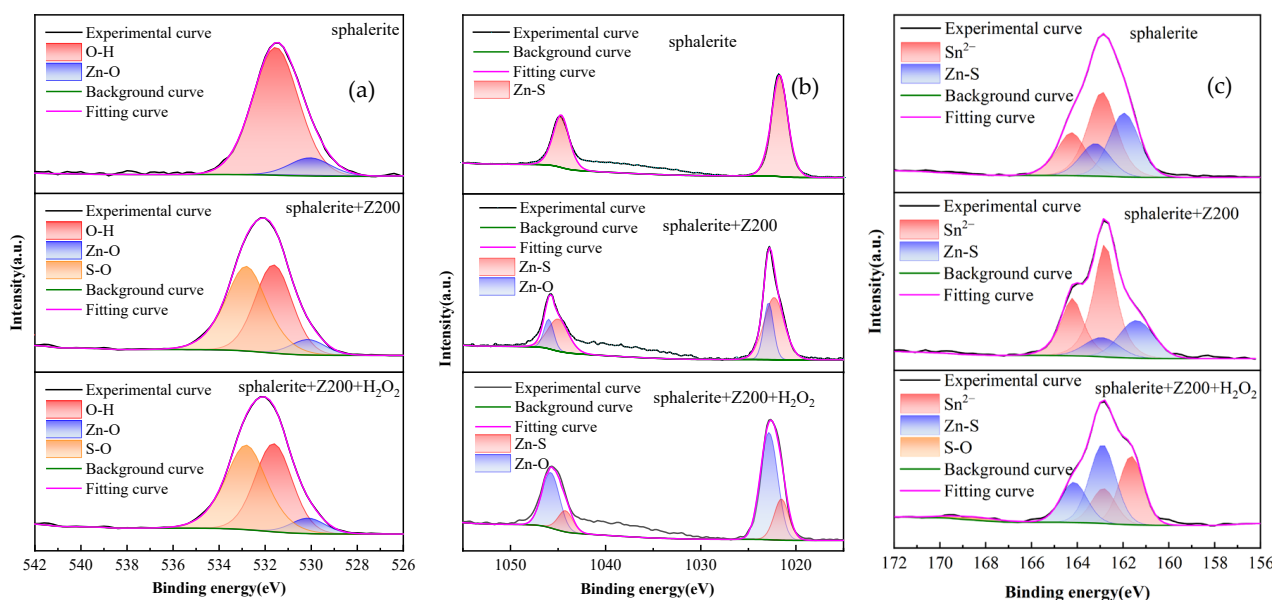
**Figure 8.** XPS spectra of O 2p (a), Zn 2p (b), and S 2p (c) on the Cu-activated sphalerite surface before and after reaction with Z-200 and Z-200 +H₂O₂.

Table 5. Percentage of O species on the Cu-activated sphalerite surface.

Samples	Zn–O		O–H		S–O	
	B.E./eV	At.	B.E./eV	At.	B.E./eV	At.
Cu-activated sphalerite	530.06	11.43	531.54	88.52	-	0.00
Cu-activated sphalerite+Z-200	530.50	31.25	531.78	52.74	533.00	16.01
Cu-activated sphalerite+H ₂ O ₂ +Z-200	530.13	6.49	531.63	40.16	532.82	44.77

Table 6. Percentage of Zn species on the Cu-activated sphalerite surface.

Samples	Zn–S		Zn–O	
	B.E./eV	At.%	B.E./eV	At.%
Cu-activated sphalerite	1021.72	100.00	-	0.00
Cu-activated sphalerite+Z-200	1021.31	61.54	1022.17	38.46
Cu-activated sphalerite+H ₂ O ₂ +Z-200	1021.53	24.91	1022.84	75.09

Table 7. Percentage of S species on the Cu-activated sphalerite surface.

Samples	Zn–S		S _n ^{2−}		S–O	
	B.E./eV	At.%	B.E./eV	At.%	B.E./eV	At.%
Cu-activated sphalerite	161.21	42.96	162.05	57.04	-	0.00
Cu-activated sphalerite+Z-200	160.74	31.44	161.94	68.56	-	0.00
Cu-activated sphalerite+H ₂ O ₂ +Z-200	161.64	43.24	162.89	53.63	168.31	3.12

Figure 8a shows two fitted O 1s peaks for Cu-activated sphalerite at 530.09 eV and 531.54 eV, corresponding to Zn–O and O–H, respectively [36]. After adding Z-200, a new peak emerges at 533.00 eV (S–O), while the Zn–O atomic concentration decreases and O–H increases, likely due to the adsorption of Z-200. The presence of functional groups such as thiocarbonyl (C=S) and ether oxygen (–O–) in Z-200 contributes to the increased surface concentrations of sulfur and oxygen. When Cu-activated sphalerite interacts with Z-200 and H₂O₂, Zn–O and O–H concentrations drop significantly and S–O rises sharply, indicating strong surface oxidation by H₂O₂, resulting in the formation of hydroxyl and sulfoxy compounds [37].

In Figure 8b, the Cu-activated sphalerite shows Zn 2p_{3/2} and Zn 2p_{1/2} main peaks, with Zn 2p_{3/2} at 1021.72 eV corresponding to Zn–S; no other Zn species are detected [38]. After Z-200 treatment, a new Zn–O peak appears at 1022.17 eV with an atomic concentration of 38.46%, while Zn–S decreases to 61.54% and its binding energy shifts by −0.41 eV, indicating that surface Zn atoms participate in chemical reactions [39]. When Cu-activated sphalerite interacts with both Z-200 and H₂O₂, the concentration of Zn–O atoms rises significantly to 75.09%, demonstrating that H₂O₂ strongly oxidizes the sphalerite surface, forming a large amount of zinc oxide [40].

Figure 8c shows the fitted S 2p spectra for Cu-activated sphalerite. Two peaks appear at 161.24 eV and 162.05 eV, corresponding to Zn–S and S_n^{2−} species, with atomic concentrations of 42.96% and 57.04%, respectively [41,42]. After Z-200 treatment, the binding energies of Zn–S and S_n^{2−} shift downward by 0.47 eV and 0.11 eV, respectively, while atomic concentrations of Zn–S decreases and S_n^{2−} increases, likely due to Z-200 adsorption, consistent with the O 1s analysis. When Z-200 and H₂O₂ are both applied, a new peak

at 168.31 eV appears, attributed to S–O. Combined with the O 1s results, this indicates that H₂O₂ induces the formation of sulfate species on the sphalerite surface, albeit at a low concentration of 3.12% [43].

4. Conclusions

In the flotation separation of copper–zinc mixed ores, the dissolved copper ions in the pulp undesirably activate sphalerite, making the floatability of copper and zinc ores similar and difficult to separate. In this study, H₂O₂ was identified as an efficient depressant for copper–zinc separation, capable of replacing conventional sulfate-based depressants without pH adjustment, featuring a simple reagent scheme and no harmful byproducts, in line with green beneficiation principles. Through pure mineral flotation, contact angle tests, surface adsorption analysis, zeta potential analysis, and XPS analysis, the mechanism of H₂O₂ on chalcopyrite and sphalerite was investigated. The main findings are summarized as follows:

(1) Both Cu-activated sphalerite and chalcopyrite exhibit good floatability. After adding H₂O₂, Cu-activated sphalerite is strongly depressed, while chalcopyrite is minimally affected. In the flotation of mixed ores, when the dosage of the collector Z-200 was 10 mg·L^{−1} and that of the depressant H₂O₂ was 8 mmol·L^{−1}, a copper concentrate with a Cu grade of 29.95% and a recovery of 87.30% was obtained, along with a zinc concentrate containing 54.12% Zn and a recovery of 91.02%. These results indicate a significant separation between copper and zinc under the given conditions.

(2) H₂O₂ addition greatly increases the hydrophilicity of Cu-activated sphalerite but has little effect on chalcopyrite. This is because H₂O₂ oxidized the Cu-activated sphalerite, leading to the formation of hydrophilic oxides that covered the mineral surface, while the surface of chalcopyrite remained hydrophobic. As a result, the surface property difference between copper-activated sphalerite and chalcopyrite was enhanced, enabling their flotation separation.

(3) H₂O₂ exerts a strong oxidative effect on Cu-activated sphalerite. After H₂O₂ addition, the O atomic concentration increases significantly while Zn and S concentrations decrease concurrently. This is due to surface oxidation by H₂O₂ producing metal oxides and sulfate species that cover the mineral surface, and the reduced C concentration further confirms that H₂O₂ inhibits Z-200 adsorption.

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Conflicts of Interest: Bin Han, Haitao Fu and Zhiming Lu are employed by Yunnan Hualian Zinc and Indium Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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