

Article

Enhancement of the Collectorless Flotation of Oxidized Chalcopyrite by Quartz Particles

Lei Sun, Dianshun Li, Feng Jiang *, Yang Cao, Xin Wang, Miaoxiang Ai and Wei Sun

School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China; sunlei@csu.edu.cn (L.S.); 235611042@csu.edu.cn (D.L.); caoyang@csu.edu.cn (Y.C.); xin.w_csu@csu.edu.cn (X.W.); aimiaoxiang@csu.edu.cn (M.A.); sunmenghu@csu.edu.cn (W.S.)

* Correspondence: feng_jiang@csu.edu.cn; Tel.: +86-731-88830482

Abstract

The collectorless flotation of chalcopyrite has the potential to facilitate the efficient separation of Cu–Mo and Cu–Ni ores while reducing reagent consumption. This process relies on the natural hydrophobicity of the chalcopyrite surface, which can be adversely affected by surface oxidation. Quartz, a ubiquitous gangue mineral in chalcopyrite flotation systems, is widely present throughout flotation circuits. In this study, the effects of quartz particles of varying sizes on the surface properties and flotation behavior of chalcopyrite under different oxidation conditions were systematically investigated through micro-flotation experiments, contact angle measurements, X-ray photoelectron spectroscopy (XPS), and particle size analysis. The results indicate that hydrophilic iron (oxy)hydroxide species readily form on oxidized chalcopyrite surfaces, leading to reduced floatability. The presence of quartz particles was associated with a reduction in the abundance of surface iron (oxy)hydroxide species and an improvement in collectorless flotation performance. These findings suggest that interactions between quartz and chalcopyrite may mitigate the adverse effects of surface oxidation. They also highlight the potential of collectorless pre-flotation strategies for copper ore processing.

Keywords: chalcopyrite; quartz; collectorless flotation; surface oxidization; scrubbing

1. Introduction

Copper is widely used in industry because of its excellent electrical and thermal conductivity, good processability, and corrosion resistance [1,2]. Approximately 250 copper-bearing minerals have been identified in nature. Among these, copper sulfides, mainly chalcopyrite, are currently the primary source of copper for industrial extraction [3].

In the industrial processing and utilization of chalcopyrite, flotation stands as one of the most predominantly employed methods. Typically, collectors such as xanthates, dithiophosphates, and thionocarbamates are introduced during the flotation process to enhance the surface hydrophobicity of the mineral [4–6]. However, during the flotation separation of chalcopyrite from molybdenite or pentlandite, the unselective adsorption of collectors on all mineral surfaces necessitates an increased dosage of depressants, or even the incorporation of a de-reagentizing stage, thereby exacerbating the difficulty of separation [7]. Conversely, collectorless flotation offers a viable approach to partially circumvent this challenge [8]. An industrial trial [9] demonstrated that implementing collectorless flotation as the primary stage in the flotation circuit can elevate the grade of the

Academic Editor: Luis Vinnett

Received: 13 May 2026

Revised: 24 June 2026

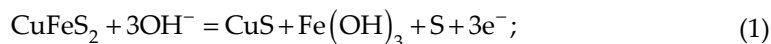
Accepted: 29 June 2026

Published: 30 June 2026

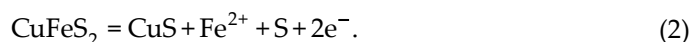
Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\) license](https://creativecommons.org/licenses/by/4.0/).

molybdenum concentrate by 2.78% compared to conventional processes, while simultaneously reducing daily reagent consumption by over 10%. Consequently, it represents a highly feasible strategy that delivers both economic benefits and product quality advantages.

The collectorless flotation of chalcopyrite capitalizes on its self-induced floatability, a property that originates from the elemental sulfur and polysulfides generated during oxidation. The corresponding electrochemical reaction equations are presented as follows [10,11]: Under alkaline conditions:



Under acidic conditions:



Under alkaline conditions, the surface oxidation of chalcopyrite results in the formation of a hydrophilic iron hydroxide layer, thereby deteriorating its floatability. According to the model proposed by Buckley [12], chalcopyrite oxidized in alkaline solutions exhibits a stratified structure: the outermost layer consists of iron (oxy)hydroxide, the intermediate layer is composed of an iron-deficient copper sulfide, and the innermost layer is the unreacted bulk mineral. Consequently, the presence of surface iron (oxy)hydroxide emerges as one of the critical factors governing the flotation of chalcopyrite.

Quartz (SiO_2) is the most ubiquitous gangue mineral associated with chalcopyrite ores, characterized by its high hardness and resistance to comminution. As high-grade copper resources continue to deplete, mineral processing plants are compelled to increase grinding fineness to achieve adequate mineral liberation [13]. Furthermore, extensive moraine deposits (sediments resulting from glacial activity) are prevalent on the surface of certain copper mining regions [14], which contain abundant fine quartz particles. These fine quartz particles are conventionally perceived to exert detrimental effects on chalcopyrite flotation; they not only report to the flotation froth via mechanical entrainment, thereby degrading the concentrate grade [15], but also deteriorate the floatability of chalcopyrite through mechanisms such as slime coating [16] and competitive collector adsorption [17].

However, the present study reveals a counterintuitive phenomenon: under collectorless conditions, quartz particles actually promote the flotation of chalcopyrite. Through single-mineral flotation experiments and a comprehensive suite of surface analysis techniques, we demonstrate that quartz particles serve to “scrub” the chalcopyrite surface, effectively stripping away the hydrophilic overlayer, which consequently leads to a significant enhancement in its flotation recovery. These findings provide robust theoretical support for the integration of a collectorless flotation circuit in industrial operations.

2. Materials and Methods

2.1. Materials

The chalcopyrite and quartz samples used in this study were collected from Jiangxi Province, China. The phase composition and chemical constituents were characterized via X-ray diffraction (XRD, D8 ADVANCE, BRUKER Corporation, Karlsruhe, Germany) and chemical analysis, with the corresponding XRD patterns illustrated in Figure 1. Chemical assays revealed Cu and Si contents of 32.98% and 45.42% for the chalcopyrite and quartz samples, respectively. Based on these results, the calculated mineral purities were 95.2% for chalcopyrite and 97.2% for quartz, both of which satisfy the requirements for single-mineral experimental studies.

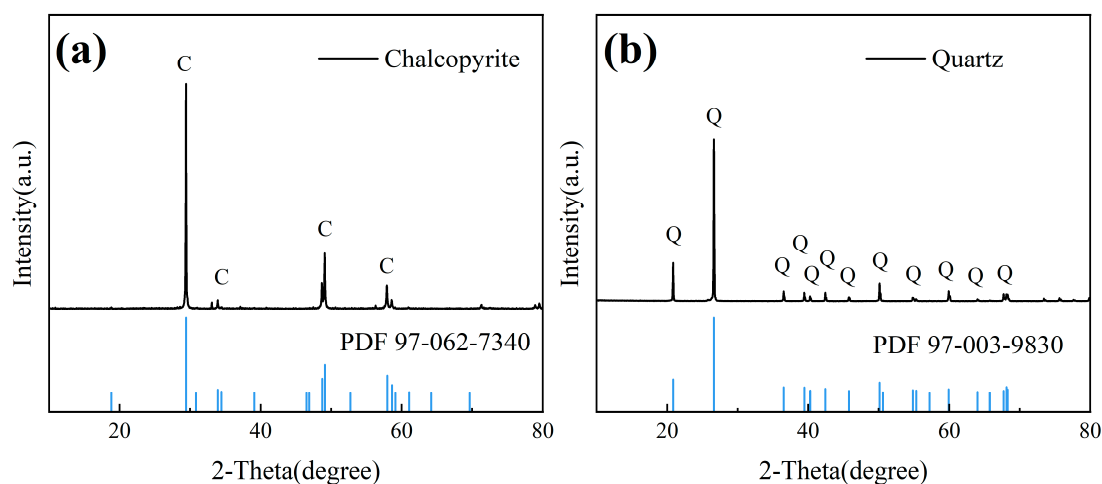


Figure 1. XRD spectra of test samples: (a) chalcopyrite; (b) quartz.

The sample preparation procedure was as follows: First, the chalcopyrite and quartz ores were crushed to -2 mm using a jaw crusher. The crushed products were then ground in a laboratory pot mill using alumina ceramic balls as the grinding media. A $74\ \mu\text{m}$ standard sieve was used for size control; the oversize fraction was returned to the mill for re-grinding until all of the material passed through the sieve. For chalcopyrite, the $-74\ \mu\text{m}$ product was further screened at $37\ \mu\text{m}$ to obtain two size fractions of $-74+37\ \mu\text{m}$ and $-37\ \mu\text{m}$. For quartz, the $-74\ \mu\text{m}$ product was classified by gravity sedimentation. By controlling the settling time, two fractions with equivalent Stokes diameters of $-10\ \mu\text{m}$ and $-74+40\ \mu\text{m}$ were obtained. All crushing, grinding, sieving, and classification procedures were conducted under ambient atmospheric conditions and completed within one day. Freshly prepared chalcopyrite powder samples were then stored under vacuum conditions prior to further analyses to minimize further surface oxidation. The particle-size distributions of the final fractions were determined using a Particle-size Analyzer (BT-9300ST, Better-size Instruments Ltd., Dandong, China), and the results are shown in Figure 2.

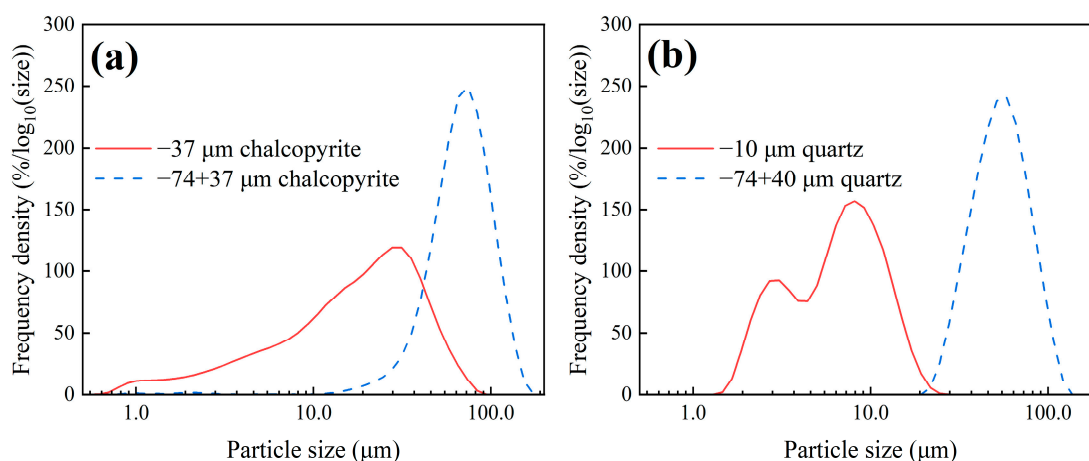


Figure 2. Particle-size distributions of the prepared chalcopyrite (a) and quartz (b) samples.

2.2. Reagents

Terpineol (AR; Xilong Scientific Co., Ltd., Shantou, China) was used as the frother. Sodium hydroxide (NaOH, AR; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was used for pH adjustment in the flotation tests. Potassium dihydrogen phosphate and anhydrous disodium hydrogen phosphate (both AR; Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China) were used to prepare the buffer solutions.

Potassium chloride (AR; Shanghai Titan Scientific Co., Ltd., Shanghai, China) was used as both the supporting electrolyte and the salt bridge filling solution. Additionally, sodium hexametaphosphate (Reagent grade; Shandong Keyuan Biochemistry Co., Ltd., Jinan, China) was used as a dispersant. Deionized water with a resistivity exceeding 16 MΩ·cm was used throughout all experimental procedures.

2.3. Preparation of Surface-Oxidized Chalcopyrite

To meet the sample requirements of the various experiments, two oxidation procedures were employed to prepare oxidized chalcopyrite, as illustrated in Figure 3. Powdered samples were used for flotation tests, X-ray photoelectron spectroscopy (XPS) analyses, and microscopic particle-size measurements, whereas bulk samples were used for XPS, scratch testing, contact angle measurements, and electrochemical impedance spectroscopy (EIS).

The powdered chalcopyrite was oxidized by natural air oxidation. Portions of the -74 $+37$ μm and -37 μm size fractions were placed in ceramic dishes and exposed to air at room temperature for 30 days. To prevent dust contamination while allowing air exchange, the containers were covered with plastic film containing approximately 10–20 uniformly distributed perforations with diameters of about 1–2 mm. During the oxidation period, the samples were homogenized every three days by 3–4 rounds of coning and mixing to promote a more uniform exposure of particles to atmospheric conditions. In addition, the samples were spread in a thin layer with a thickness of approximately 3–5 mm to minimize the influence of sample depth on the extent of oxidation.

The bulk chalcopyrite samples were subjected to electrochemical oxidation. Initially, the specimens were sequentially ground using abrasive papers (240 to 5000 grit) and subsequently polished to a mirror finish utilizing 500 nm and 20 nm alumina powders. The experiments were conducted in a conventional three-electrode cell configuration: the polished chalcopyrite served as the working electrode with an exposed surface area of 1 cm², a saturated calomel electrode (SCE) was employed as the reference electrode, and a graphite electrode acted as the counter electrode. The electrolyte consisted of a mixed solution comprising 0.1 mol/L KCl and a phosphate buffer (0.025 mol/L KH₂PO₄ and 0.025 mol/L Na₂HPO₄, pH 6.86). A constant potential of 650 mV (vs. the standard hydrogen electrode, SHE) was applied utilizing an electrochemical workstation (Jiangsu Donghua Analytical Instrument Co., Ltd., Jiangsu, China). The potentiostatic oxidation was terminated once a cumulative charge of 25 mC was attained. Subsequently, the samples were thoroughly rinsed with deionized water and dried prior to further analysis.

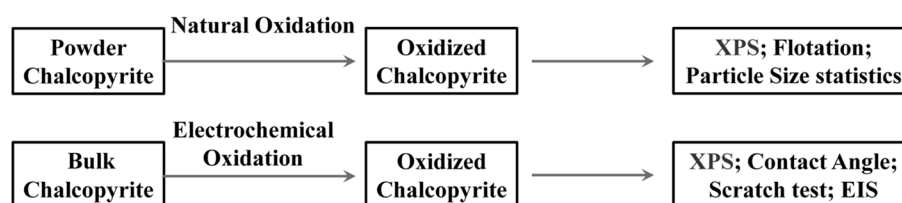


Figure 3. Schematic diagram of the two oxidation procedures.

2.4. Flotation Experiment on Pure Minerals

Flotation tests were carried out in an XFG-II5-35 g self-aerated flotation machine (Jilin Prospecting Machinery Plant, Changchun, China) at an impeller speed of 1800 r/min. The experimental procedure was as follows: First, an appropriate volume of NaOH solution and either 1.0 g of a single mineral (chalcopyrite or quartz) or 2.0 g of a mixed-mineral sample (chalcopyrite-to-quartz mass ratio of 1:1) was added to a 40 mL flotation cell and conditioned for 2 min to ensure adequate dispersion. The pulp pH was monitored using

a pH meter. Subsequently, a specified amount of pine oil solution was added, and the total pulp volume (NaOH solution plus pine oil solution) was adjusted to 36 mL, followed by 1 min of further conditioning. After conditioning, the pulp pH was checked again and adjusted, if necessary, to maintain the pulp pH at approximately 8.0 before flotation. Flotation was then conducted for 3 min, during which the froth was scraped every 10 s. Finally, the collected concentrate and tailings were separately filtered, dried, and weighed. For the single-mineral flotation tests of chalcopyrite, the recovery was calculated from the masses of the concentrate and tailings according to the following equation:

$$\text{Recovery}(\%) = \frac{m_{\text{float}}}{m_{\text{float}} + m_{\text{tailings}}} \times 100\%; \quad (3)$$

For flotation tests on chalcopyrite–quartz mixtures, the Cu contents of the concentrate and tailings were determined using a DPO-6000 handheld XRF analyzer (Innov-X Systems Inc., Boston, MA, USA), and the chalcopyrite recovery was then calculated from the Cu grades according to the following expression:

$$\text{Recovery}(\%) = \frac{m_{\text{float}} \cdot g_{\text{float}}}{m_{\text{float}} \cdot g_{\text{float}} + m_{\text{tailings}} \cdot g_{\text{tailings}}} \times 100\%. \quad (4)$$

To evaluate the reliability of the XRF method, the relationship between the XRF results and the compositions of the synthetic mineral mixtures is provided in Appendix A, Figure A1.

2.5. Flotation Experiments on Ore Samples

Ore flotation tests were conducted using a 3 L XFD-63 single-stage flotation cell. Prior to flotation, 1 kg of crushed ore was ground in a stainless-steel ball mill at 66 wt% solids to achieve a particle fineness of 65% passing 200 mesh. The ground slurry was transferred to the flotation cell, resulting in a pulp density of approximately 33 wt% solids. During flotation, MCO, a hydrocarbon oil collector, was used as the collector; lime was used as the depressant; and HCCL, an alcohol-based frother, was used as the frother. Reagents were added sequentially according to the experimental design, with a conditioning time of 3 min for each reagent. The air flow rate and impeller speed were maintained at 3 m³/h and 1950 r/min, respectively, throughout the flotation test. Upon completion of flotation, the concentrate and tailings products were filtered, dried, weighed, and analyzed for grade, and the flotation recovery was calculated based on the mass and grade data.

2.6. Particle Size Statistics

Microscopic particle-size analysis of the mineral samples was performed using an NEXCAM-T20 optical microscope (Ningbo Yongxin Optics Co., Ltd., China). The experimental procedure was as follows: A 0.05 g portion of the mineral sample and 0.25 g of the dispersant sodium hexametaphosphate were placed in a beaker, followed by the addition of 50 mL of deionized water. The suspension was then magnetically stirred at 800 r/min for 5 min to achieve adequate particle dispersion. A rubber-tipped dropper was used to collect an aliquot from the mid-depth of the suspension, which was then transferred onto a glass slide. Images were subsequently captured under the microscope using a five-point field selection method. Particle-size statistics were obtained from the images using ImageJ software (V1.54).

2.7. Contact Angle Measurements

The contact angle was measured using a JY-82C contact angle meter (Chengde Jinhe Instrument Manufacturing Co., Ltd., Chengde, China) with deionized water. The droplet morphology was captured, and the contact angle was determined using the height-width

method. For each specimen, the arithmetic mean of three independent measurements was used as the final result.

2.8. XPS Analysis

The XPS sample preparation was as follows: the fresh and oxidized powdered chalcopyrite samples were used directly for measurements, whereas the bulk chalcopyrite samples were used after electrochemical oxidation. The other powdered samples were treated under simulated flotation conditions: either 1.0 g of chalcopyrite single mineral or a mixture consisting of 1.0 g chalcopyrite and 1.0 g quartz was added to the flotation cell together with 36 mL of NaOH solution. The slurry pH was monitored using a pH meter and maintained at approximately 8.0 during conditioning at 1800 r/min for 5 min. The slurry was then filtered and dried under low-temperature vacuum prior to XPS measurements.

XPS measurements were performed on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer (Thermo Scientific Co., Waltham, MA, USA). Al K α radiation was employed as the excitation source, and the vacuum in the analysis chamber was maintained at better than 2.0×10^{-7} mbar. The operating voltage and filament current were 12 kV and 6 mA, respectively. The pass energy and step size for the narrow-scan spectra were 50 eV and 0.1 eV, respectively. A low-energy electron flood gun was used during all measurements to compensate for surface charging effects. All binding energies were calibrated with respect to the C 1s peak at 284.8 eV.

2.9. Surface Treatment of Bulk Chalcopyrite via Stirring

The bulk chalcopyrite samples were secured at a designated position on the inner wall of the flotation cell using a 3D-printed holder (Figure 4). Subsequently, 30 mL of de-ionized water was added to the cell, and the system was stirred at a high speed of 1800 rpm for 5 min. During this process, 1.0 g of quartz particles (size fraction: $-74 +40 \mu\text{m}$) was either added or omitted, depending on the specific experimental conditions. Following stirring, the chalcopyrite samples were removed and thoroughly rinsed with deionized water to remove any residual quartz particles from the surface prior to subsequent characterization.

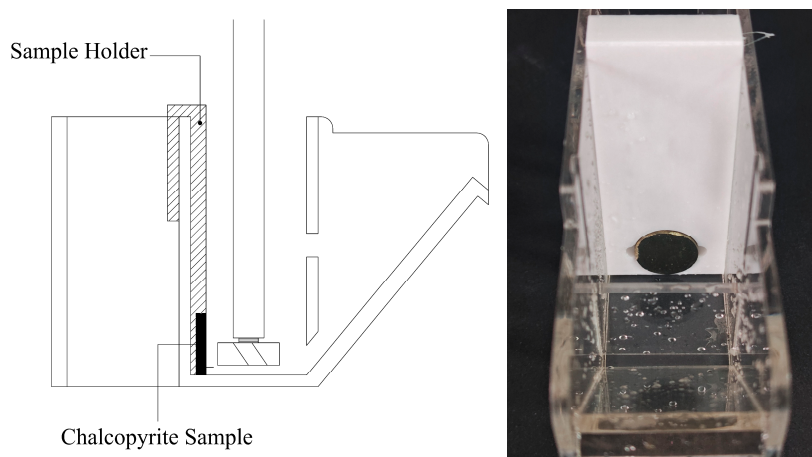


Figure 4. Schematic diagram and digital photograph of the sample holder.

2.10. Electrochemical Impedance Spectroscopy (EIS)

The same apparatus and electrolyte system from the electrochemical oxidation process were used. For the EIS measurements, the frequency range was set from 10^{-2} to 10^4 Hz, with a sinusoidal perturbation amplitude of 10 mV. Prior to the measurements, the

open-circuit potential (OCP) of the working electrode was monitored. The impedance measurements were conducted only after the system potential had reached a quasi-steady state, thereby ensuring the stability of the experimental environment and the reliability of the acquired data.

3. Results and Discussion

3.1. Analysis of Surface Composition of Powdered Chalcopyrite Before and After Oxidation

X-ray photoelectron spectroscopy (XPS) was used to record the Cu, Fe, S, and O core-level spectra of fresh and oxidized powdered chalcopyrite samples. The spectra were deconvoluted by peak fitting. The fitted components are shown in Figure 5, and the relative contents of the different species are summarized in Table 1. During the fitting procedure, the binding energies of the various Cu, Fe, S, and O species were selected with reference to previous XPS studies on chalcopyrite: Cu [18]; Fe [19]; S [20,21]; O [22,23]. The literature values were used as references for species identification, and the fitted binding energies were found to be within the ranges commonly reported for the corresponding species.

For ease of interpretation, the Fe and S species in Table 1 were grouped into second- and third-level categories. The third-level categories correspond to the basic units used in the peak fitting, whereas the second-level categories were defined to meet the needs of the subsequent analysis: FeOOH, Fe₂(SO₄)₃ and their associated satellite peaks were grouped into the “Fe–O” category, whose proportion reflects the degree of Fe oxidation. Sulfur species such as S₂^{2−}, S_n^{2−} and S⁰, which have closely spaced binding energies and multiple oxidation states that are difficult to distinguish unambiguously, were collectively classified as “intermediate oxidation states”.

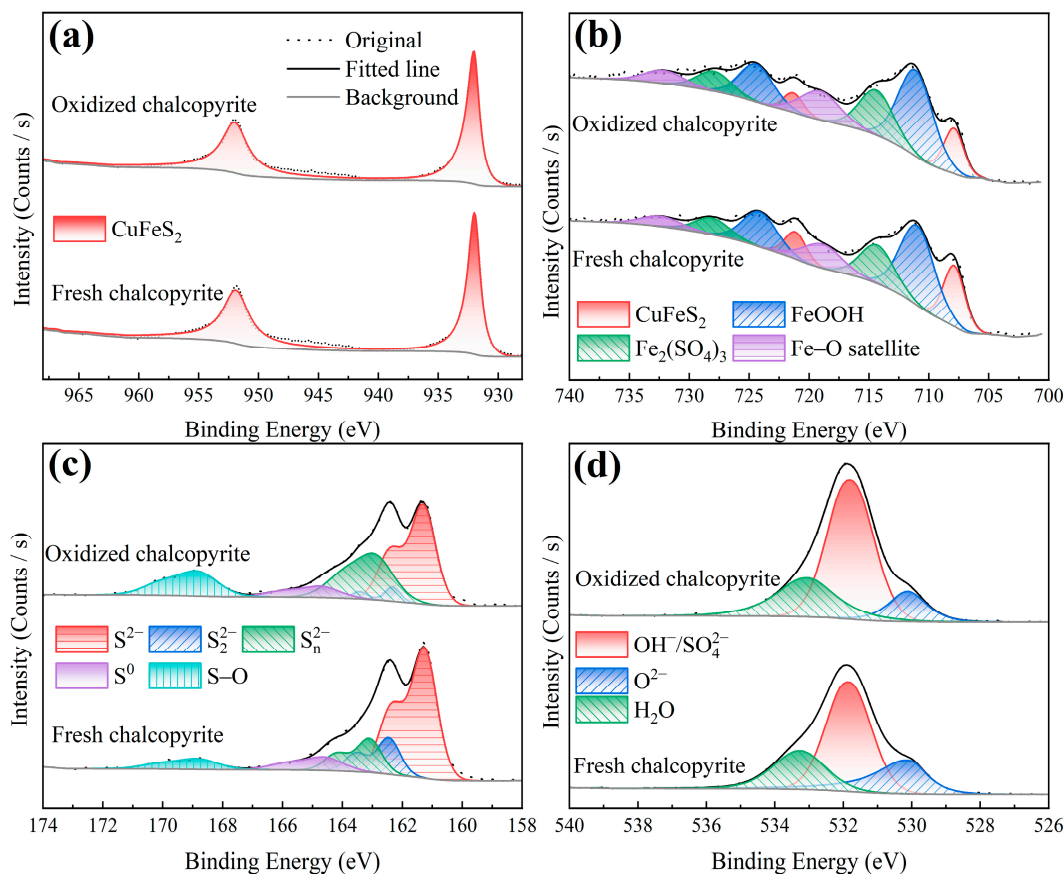


Figure 5. Fitted XPS spectra of oxidized and fresh powdered chalcopyrite: (a) Cu 2p; (b) Fe 2p; (c) S 2p; (d) O 2s.

Table 1. Elemental contents obtained from XPS peak fitting of fresh and oxidized powdered chalcopyrite.

Elem.	Atomic % *		Second-Level Category	Atomic %		Third-Level Category	Atomic %		BE (ev) **			
	Fresh Oxidized			Fresh Oxidized			Fresh Oxidized		Fresh Oxidized			
Cu	16.4	14.5				CuFeS ₂	100.0	100.0	932.0	932.0		
Fe	14.6	19.9	Fe–S	20.5	8.9	CuFeS ₂	20.5	8.9	707.9	707.9		
					FeOOH	43.6	60.1	711.0	711.0			
			Fe–O	79.5	91.1	Fe ₂ (SO ₄) ₃	21.0	19.3	714.3	714.3		
					Fe–O satellite	14.9	11.7	718.9	719.2			
S	33.1	28.8	S ²⁻	56.4	44.5	S ²⁻	56.4	44.5	161.3	161.3		
					S ₂ ²⁻	14.3	4.1	162.5	162.3			
			Intermediate states	36.8	38.9	S _n ²⁻	14.3	27.6	163.1	162.9		
					S ⁰	8.2	7.3	164.6	164.7			
					S–O	6.9	16.6	S–O	6.9	16.6	168.8	168.8
					O ²⁻	22.7	12.0	530.1	530.1			
O	35.9	36.8			OH-/SO ₄ ²⁻	54.0	62.6	531.8	531.8			
					H ₂ O	23.3	25.4	533.3	533.0			

* The atomic % in the first-level category is expressed as a percentage of the total amount of the element, whereas the atomic % in the second- and third-level categories is expressed as a percentage of that element. ** The binding energies (BEs) of the 2p orbitals are represented by the binding energy of the 2p_{3/2} component.

Table 1 presents the relative elemental concentrations of Cu, Fe, S, and O on the surfaces of the fresh and oxidized chalcopyrite samples. It is evident that, following oxidation, the relative concentrations of Fe and O on the sample surface increased from 14.6% and 35.9% to 19.9% and 36.8%, respectively, compared to the fresh chalcopyrite. Conversely, the relative concentrations of S and Cu exhibited a corresponding decrease. This compositional variation trend is in good agreement with the findings reported by Brion [24].

Table 1 also presents the quantitative results for the various chemical states of each element. During the oxidation process, the chemical state of Cu exhibited no significant alteration, remaining predominantly in the form of Cu⁺. Conversely, the relative concentration of Fe–O species within the Fe element increased significantly from 79.5% to 91.1%. For the S element, the content of intermediate oxidation states rose from 36.8% to 38.9%, while the proportion of S–O species increased from 6.9% to 16.6%. Similarly, the proportion of OH[−]/SO₄^{2−} species within the O element increased from 54.0% to 62.6%.

The above experimental results indicate that a series of surface reactions occur on chalcopyrite during oxidation: sulfur species are progressively transformed into polysulfides and sulfate species, while the released Fe ions migrate to the mineral surface and form products such as ferric oxyhydroxide and ferric sulfate.

3.2. Preparation and Surface Compositional Analysis of Oxidized Bulk Chalcopyrite

To prepare bulk chalcopyrite samples capable of simulating a naturally oxidized surface state, linear sweep voltammetry (LSV) was performed on the polished electrodes. The resulting voltammogram is illustrated in Figure 6a. Based on the characteristics of the polarization curve, it can be divided into three typical regions:

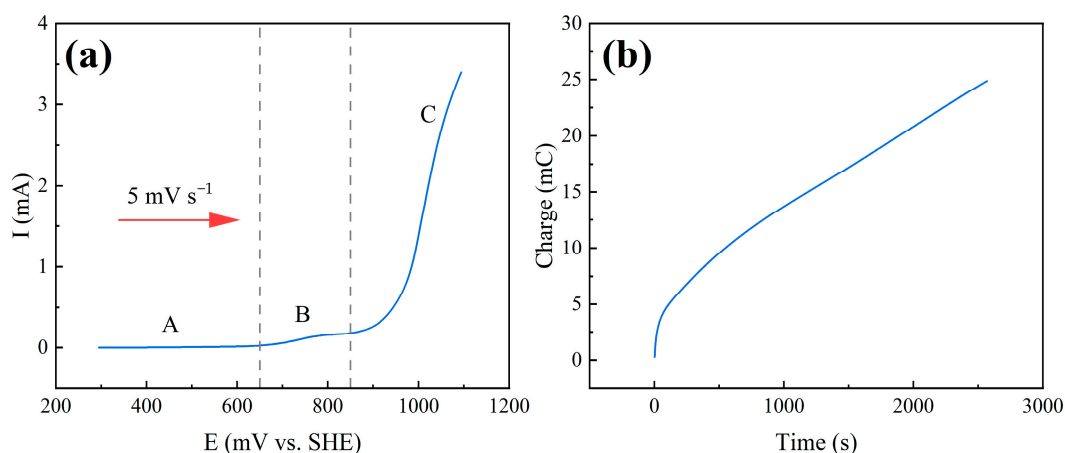
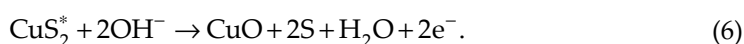
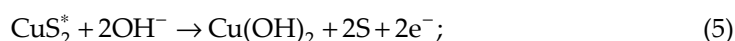


Figure 6. (a) Linear sweep voltammogram of chalcopyrite and (b) the chronocoulometric response at an applied potential of 650 mV.

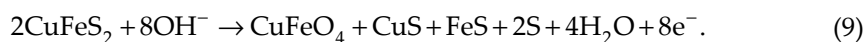
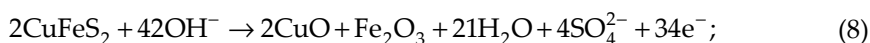
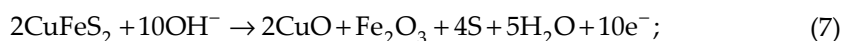
Region A (OCP to 650 mV): Only a marginal anodic current was observed in this region, which is primarily attributed to the gradual formation of iron (oxy)hydroxide (FeOOH) and iron-deficient chalcopyrite ($\text{CuFe}_{(1-x)}\text{S}_2$) [25].

Region B (650–850 mV): A shallow peak is observed in this region, which is generally attributed to the oxidation of surface Cu species, namely the oxidation of iron-deficient copper sulfide phases [25,26]. The associated reactions proceed as follows [25]:



CuS_2^* denotes the limiting composition of $\text{CuFe}_{(1-x)}\text{S}$.

Region C (>850 mV): A rapid increase in anodic current is observed in this region, indicating the breakdown of the surface passive film and the vigorous oxidation of the bulk chalcopyrite. The possible reaction mechanisms include [25]:



As discussed in Section 3.1, under natural oxidation conditions, the surface oxidation of chalcopyrite primarily involves the formation of iron (oxy)hydroxide (FeOOH) and iron-deficient chalcopyrite ($\text{CuFe}_{(1-x)}\text{S}_2$), without the concurrent oxidation of Cu species. Consequently, to prepare bulk samples capable of simulating this naturally oxidized state, a constant potential of 650 mV was applied to oxidize the polished chalcopyrite surfaces, and the target cumulative charge was set to 25 mC. The corresponding charge-time (Q-t) curve recorded during the oxidation process is presented in Figure 6b.

XPS measurements and peak fitting were performed on the electrochemically oxidized chalcopyrite surface, and the resulting spectra are presented in Figure 7. As illustrated by the survey spectrum in Figure 7a, the characteristic peaks of O 1s and Fe 2p are highly pronounced on the oxidized chalcopyrite surface, whereas the signal responses of Cu and S are exceedingly weak. In addition, Na, K, and P signals were detected on the mineral surface. These elements are likely associated with species derived from the pH buffer solution used during electrochemical oxidation. The exact nature of their occurrence on the oxidized surface remains unclear and warrants further investigation.

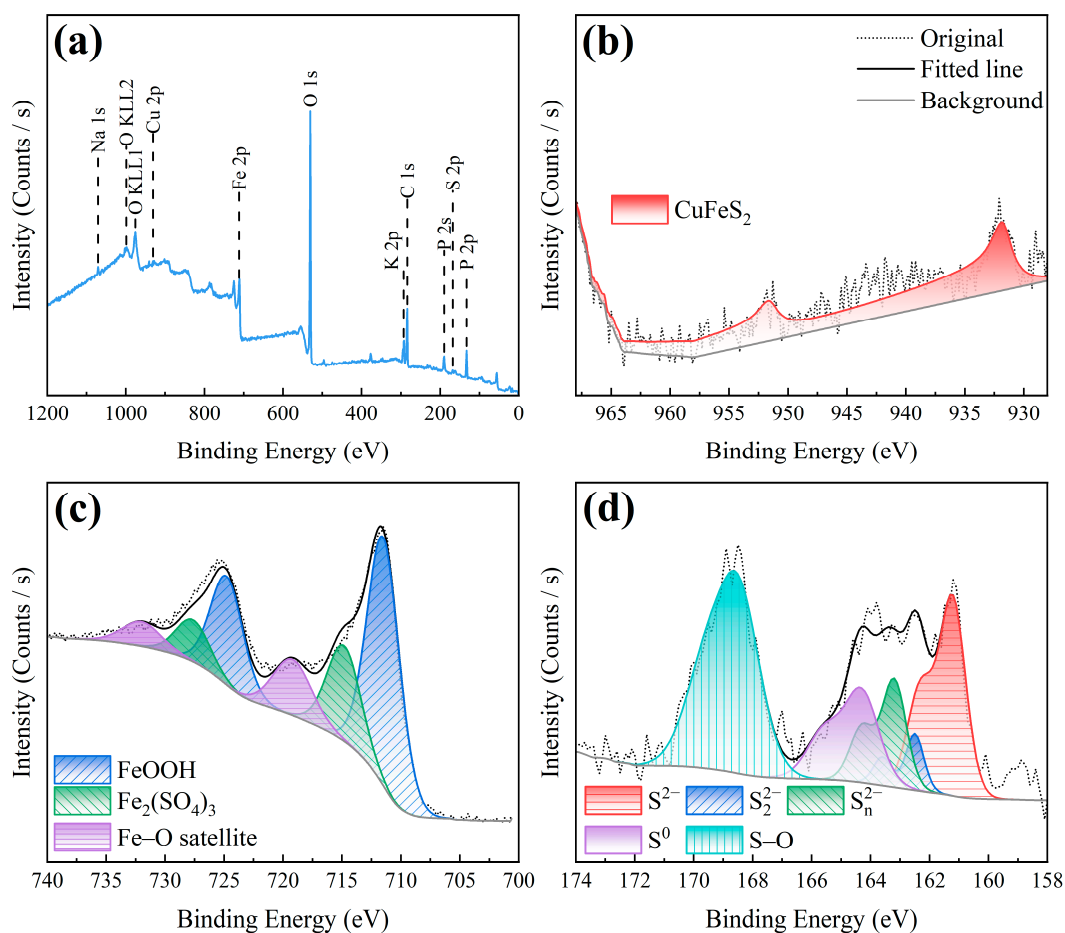


Figure 7. XPS survey spectrum of the electrochemically oxidized surface (a), and high-resolution spectra of (b) Cu 2p, (c) Fe 2p, and (d) S 2p.

The high-resolution spectra of Cu, Fe, and S are presented in Figure 7b–d. The signal response of Cu 2p is exceedingly weak, with the spectrum exhibiting pronounced background noise. In the Fe 2p spectrum, the characteristic signal assigned to the chalcopyrite matrix is no longer observable; instead, the composition consists entirely of FeOOH, $\text{Fe}_2(\text{SO}_4)_3$, and their associated satellite peaks. In the S 2p spectrum, the proportion of S–O species accounts for as much as 38.2%. This specific phase is predominantly bonded with Fe and enriched on the mineral surface, whereas the remaining intermediate sulfur species and monosulfides are primarily bonded with Cu and still reside within the bulk chalcopyrite.

XPS analysis reveals that the resulting oxidized layer is a mixture of iron (oxy)hydroxide (FeOOH) and iron-sulfur oxides. Although the oxidation depth exceeds that of natural oxidation, the phase composition remains highly analogous. Consequently, the prepared surface can be regarded as a limiting case of natural oxidation progressing into the deeper layers, thereby demonstrating strong representativeness.

3.3. Flotation Results

Figure 8 shows the variation in recovery with frother concentration for four chalcopyrite samples (−37 μm fresh, −74 +37 μm fresh, −37 μm oxidized, and −74 +37 μm oxidized) under single-mineral conditions and in mixtures with quartz. For comparison, the single-mineral flotation recovery of −10 μm quartz is also included.

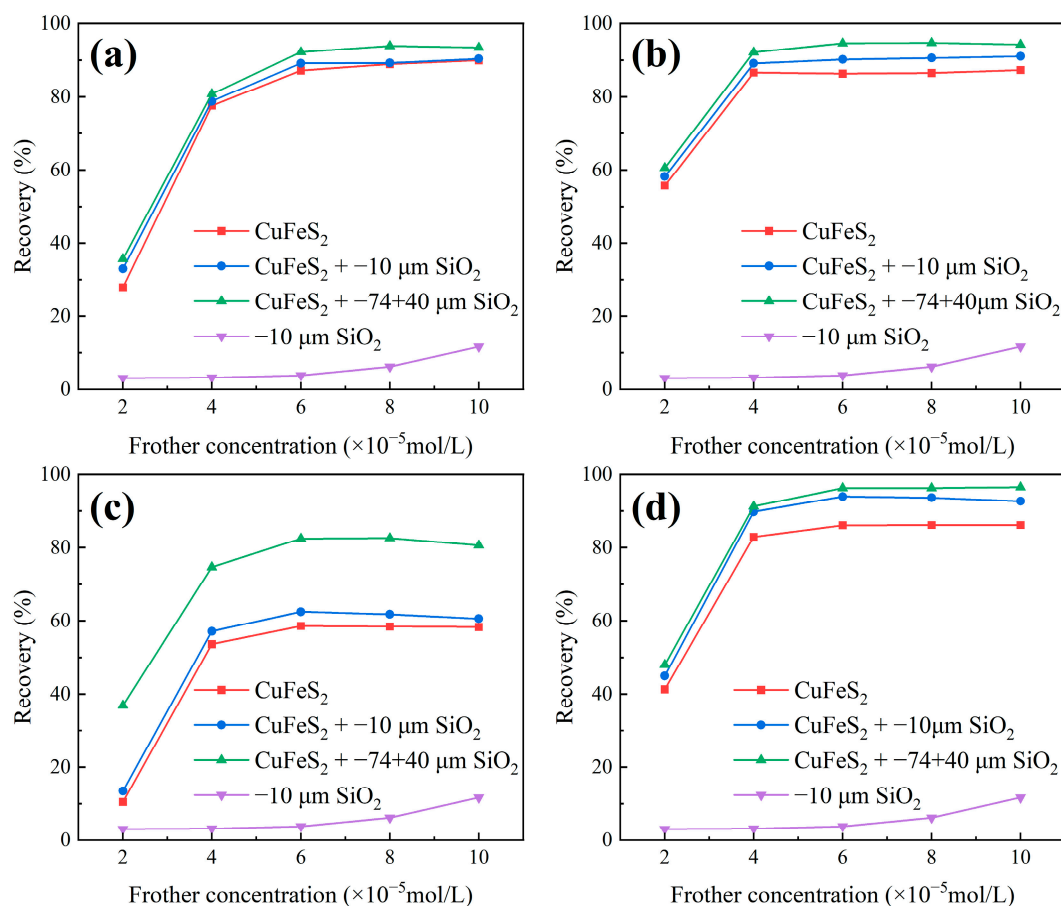


Figure 8. Recoveries of Chalcopyrite (Single/Mixed Flotation) and Quartz (Single Flotation) vs. Frother Concentration: (a) -37 μ m fresh chalcopyrite; (b) -74 +37 μ m fresh chalcopyrite; (c) -37 μ m oxidized chalcopyrite; (d) -74 +37 μ m oxidized chalcopyrite.

As shown in Figure 8, over the investigated frother concentration range, the recovery of quartz increases slightly with increasing frother concentration but overall remains low, mainly because its strongly polar surface makes it highly hydrophilic [27]. Although particle size may also affect quartz flotation, the flotation performance of quartz remained poor even for coarser particles, indicating that its strong hydrophilicity is the dominant factor limiting recovery under the investigated conditions. In contrast, the recovery of chalcopyrite initially increases and then levels off with increasing frother concentration; when the concentration exceeds 6×10^{-5} mol/L, the recovery remains at a relatively high and nearly constant level, reflecting the inherently good natural floatability of chalcopyrite.

At a frother concentration of 6×10^{-5} mol/L, a comparison of the recoveries shows that oxidation has a pronounced effect on the floatability of fine-grained chalcopyrite: for the -37 μ m fraction, the recovery decreases from 87% to 59% after oxidation, whereas for the -74 +37 μ m fraction, the recovery after oxidation still remains at around 86%.

The effect of adding quartz particles on chalcopyrite flotation varies depending on its oxidation state and particle size. For fresh chalcopyrite (Figure 8a,b), the addition of quartz at either size fraction (-74 +40 μ m or -10 μ m) only slightly improves the recovery, indicating a limited overall effect.

For oxidized chalcopyrite, a more pronounced influence is observed. For the -74 +37 μ m oxidized chalcopyrite at a frother concentration of 6×10^{-5} mol/L, the addition of -74 +40 μ m and -10 μ m quartz increases the recovery from 86% to 94% and 96%, respectively. In contrast, for the -37 μ m oxidized chalcopyrite, the addition of -74 +40 μ m quartz

markedly increases the recovery from 59% to 82%, whereas the addition of $-10\ \mu\text{m}$ quartz only results in a slight increase (from 59% to 62%).

These results indicate that the influence of quartz particles differs under different particle size conditions of chalcopyrite and oxidation states, suggesting a size-dependent interaction effect in the flotation system.

It should also be noted that the flotation results presented in Figure 8 correspond to single measurements conducted under each experimental condition. Although replicate tests were not performed, the same trends were consistently observed across the investigated frother concentration range.

3.4. Particle Size Statistics Under Microscope

Flotation tests were conducted on 1.0 g of $-37\ \mu\text{m}$ oxidized chalcopyrite, both as a single mineral and in a mixture with 1.0 g of $-74 +40\ \mu\text{m}$ quartz. Representative microscopy images of the resulting concentrates and tailings were captured. Under optical microscopy, chalcopyrite particles were readily distinguished from quartz particles because chalcopyrite appeared opaque, whereas quartz particles were transparent. Consequently, only the identified chalcopyrite particles were extracted from the microscopy images and analyzed using ImageJ software (Figure 9b–e). For the particle size analysis, the range of $0.05\text{--}210\ \mu\text{m}$ was partitioned into 12 equally spaced logarithmic intervals. The distribution frequency of each interval was calculated, and the logarithmic midpoints were connected to construct the particle size distribution curve for chalcopyrite (Figure 9a).

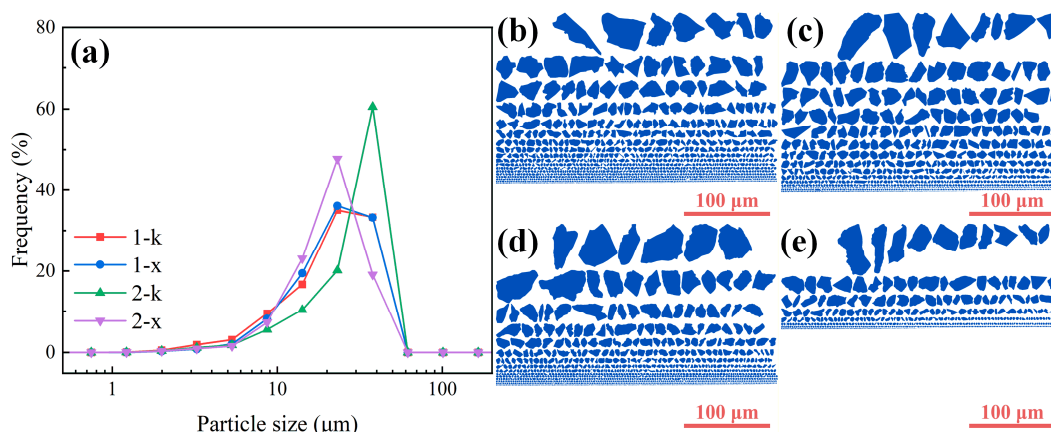


Figure 9. Particle-size distributions of chalcopyrite in the concentrates and tailings obtained without quartz (1-k, 1-x) and with quartz (2-k, 2-x) (a); (b–e) optical micrographs of samples 1-k (b), 1-x (c), 2-k (d), and 2-x (e).

As depicted in Figure 9a, in the single-mineral flotation system, the particle size distribution profiles of chalcopyrite in the concentrate (1-k) and tailings (1-x) are nearly identical, with the two curves virtually superimposing. Upon the addition of quartz particles, a pronounced restructuring of the size distributions between the products is observed: the distribution curve of the concentrate (2-k) shifts significantly toward the coarser size fraction, whereas that of the tailings (2-x) shifts toward the finer end. This demonstrates that the incorporation of quartz primarily enhances the recovery of the relatively coarser particles within the $-37\ \mu\text{m}$ chalcopyrite fraction.

This observation is consistent with the earlier result that $-74 +40\ \mu\text{m}$ quartz has a stronger promoting effect than $-10\ \mu\text{m}$ quartz, both indicating that the promoting role of quartz in chalcopyrite flotation is size-dependent; that is, both chalcopyrite and quartz must reach a certain particle size to achieve the optimum effect. This finding supports the hypothesis that quartz exerts a “scrubbing” action on the chalcopyrite surface: coarser

mineral particles possess higher kinetic energy during stirring, which facilitates more effective collisions and the removal of hydrophilic surface deposits (e.g., ferric oxyhydroxide). In contrast, ultrafine particles have insufficient kinetic energy to generate collisions strong enough to significantly modify the surface properties.

We note that, as shown in Figure 8d, $-10\ \mu\text{m}$ quartz appears to exhibit a promoting effect comparable to that of $-74 + 40\ \mu\text{m}$ quartz. Based on a reasonable assumption, relatively coarse chalcopyrite particles may possess higher kinetic energy during flotation. In this context, the presence of fine ($-10\ \mu\text{m}$) quartz particles may act as a grinding (abrasive) medium, promoting localized mechanical contact and facilitating the removal of hydrophilic surface products, thereby leading to a comparable improvement in recovery for both quartz size fractions.

3.5. XPS Analysis of the Electrochemically Oxidized Chalcopyrite

XPS was employed to record the Fe and S spectra of $-37\ \mu\text{m}$ oxidized chalcopyrite samples under three conditions: without quartz stirring, after stirring with $-10\ \mu\text{m}$ quartz, and after stirring with $-74 + 40\ \mu\text{m}$ quartz. The resulting spectra were deconvoluted by peak fitting; the fitted spectra are shown in Figure 10, while the relative contents of the different chemical states are listed in Table 2.

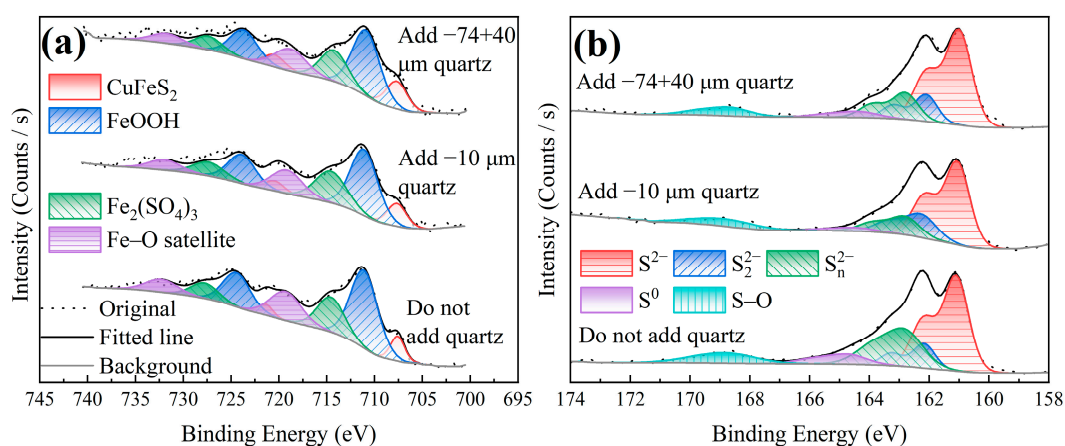


Figure 10. Fitted Fe 2p (a) and S 2p (b) XPS spectra of chalcopyrite after stirring with quartz of different particle-size fractions.

Table 2. Elemental contents obtained from XPS peak fitting of chalcopyrite after stirring with quartz of different particle-size fractions.

Second-Level Category	Atomic % *			Third-Level Category	Atomic %			BE (ev) **		
	No Quartz	$-10\ \mu\text{m}$ Quartz	$-74 + 40\ \mu\text{m}$ Quartz		No Quartz	$-10\ \mu\text{m}$ Quartz	$-74 + 40\ \mu\text{m}$ Quartz	No Quartz	$-10\ \mu\text{m}$ Quartz	$-74 + 40\ \mu\text{m}$ Quartz
Fe-S	7.8	10.9	14.6	CuFeS ₂	7.8	10.9	14.6	707.6	707.7	707.7
				FeOOH	47.9	45.5	45.6	711.1	711.1	710.9
				Fe ₂ (SO ₄) ₃	25.5	24.9	21.9	714.6	714.6	714.2
				Fe-O satellite	18.8	18.6	18.0	719.3	719.2	718.8
Intermediate states	43.2	39.7	35.3	S ²⁻	48.0	51.8	57.5	161.1	161.0	161.0
				S ₂ ²⁻	10.9	32.7	14.3	162.2	162.3	162.1
				S _n ²⁻	25.3	3.0	16.2	162.8	162.8	162.8
				S ⁰	7.1	4.1	4.8	164.7	164.3	164.3
S-O	8.8	8.5	7.2	S-O	8.8	8.5	7.2	168.6	168.6	168.6

* The atomic % values in the table are expressed as percentages of the respective elements. ** The binding energies (BEs) of the 2p orbitals are represented by the binding energy of the 2p_{3/2} component.

Table 2 shows a clear decrease in surface oxidation products when oxidized chalcopyrite is stirred with quartz. Compared with the sample without quartz, stirring with $-10\ \mu\text{m}$ quartz reduces the Fe–O fraction from 92.2% to 89.1%, whereas the fractions of the intermediate sulfur oxidation states and S–O species decrease from 43.2% to 39.7% and from 8.8% to 8.5%, respectively. When $-74\ +40\ \mu\text{m}$ quartz is used, these fractions decrease further, with Fe–O, intermediate oxidation states, and S–O species dropping to 85.4%, 35.3%, and 7.2%, respectively.

These results indicate that co-stirring with quartz effectively disrupts the oxidized layer on the chalcopyrite surface, and that $-74\ +40\ \mu\text{m}$ quartz is more effective in removing this layer than $-10\ \mu\text{m}$ quartz. This observation is consistent with the flotation and Particle size statistics results described above and further supports the proposed “quartz scrubbing” mechanism.

3.6. Surface Oxidation Film Properties of Bulk Electrochemically Oxidized Chalcopyrite

Following polarization at a constant potential of 650 mV for a cumulative charge of 25 mC, a macroscopically visible brown layer of oxidation products formed on the chalcopyrite surface. The microscopic morphology is illustrated in Figure 11a, where the upper-left and lower-right corners of the image clearly present the oxidized region and the unoxidized substrate, respectively. The observed heterogeneity is attributed to the partial coverage of the sample surface by a sealing ring during the electrochemical oxidation process, which prevented certain areas from being exposed to the electrolyte and thus inhibited oxidation. The physical structure of this oxide film is relatively loose; it can be readily scraped off mechanically, leaving distinct scratches, merely by using low-hardness (Mohs hardness 1–2) polyethylene (PE) tweezers (Figure 11b).

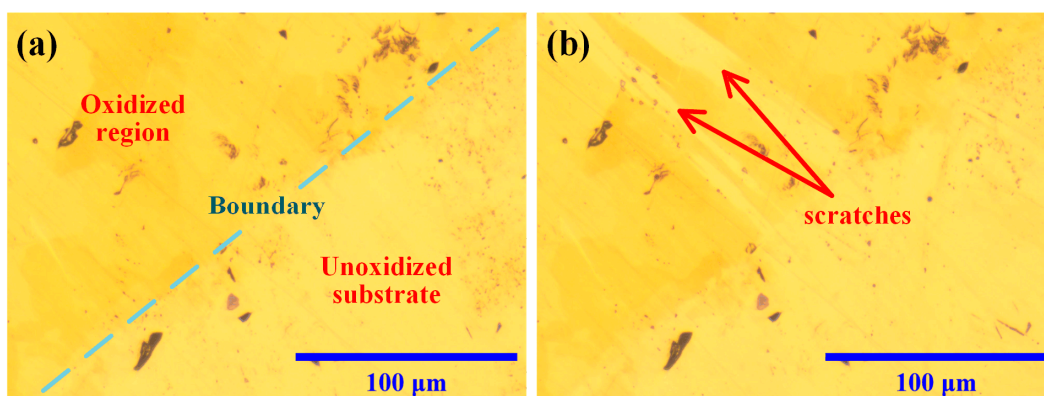


Figure 11. Optical micrographs of chalcopyrite: (a) boundary of the oxidized surface, and (b) surface scratches induced by scratching with PE tweezers.

The evolution of surface wettability on chalcopyrite prior to and following oxidation was analyzed via contact angle measurements (Figure 12). The contact angle of the pristine polished surface was 60.2° , which decreased sharply to 25.3° after oxidation, reflecting the pronounced hydrophilicity of the oxidation products. Upon subsequent removal of the oxide layer using PE tweezers, the contact angle recovered to 54.0° . These results indicate that the oxidation-induced degradation in hydrophobicity stems primarily from the overlying loose product layer; therefore, mechanical stripping of this layer allows the newly exposed chalcopyrite substrate to partially recover its original wettability.

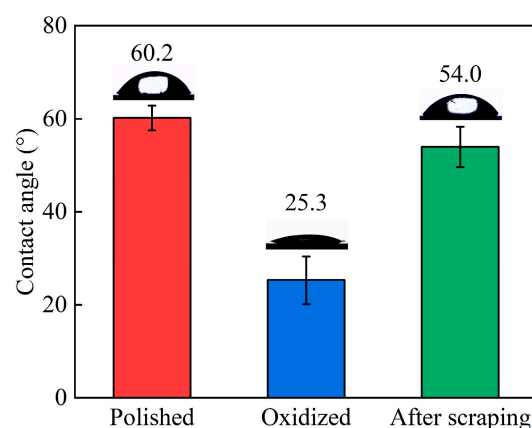


Figure 12. Contact angles of chalcopryrite subjected to different surface treatments (mean $\pm$ standard deviation): pristine polished surface, electrochemically oxidized surface, and the surface following the removal of the oxide layer.

3.7. Stirring Treatment and Electrochemical Impedance Spectroscopy of Bulk Electrochemically Oxidized Chalcopryrite

To verify the mechanical stripping effect of the flotation flow field on the chalcopryrite surface oxide layer, two parallel comparative experiments were designed. Initially, the polished and electrochemically oxidized bulk chalcopryrite specimens were fixed to the inner wall of the flotation cell. Subsequently, a $-74 \pm 40 \mu\text{m}$ quartz slurry and deionized water were separately employed as the stirring media to subject the samples to hydrodynamic scouring. Electrochemical impedance spectroscopy (EIS) measurements were conducted on the specimen surfaces at three key stages—following initial polishing, after electrochemical oxidation, and post-stirring treatment—to track the evolution of the oxide layer under varying physical interventions.

Figure 13 presents the Nyquist plots of the chalcopryrite across the different treatment stages. All datasets exhibit a single capacitive loop, with no apparent diffusion impedance observed, indicating that the kinetic process of the system is predominantly controlled by the charge-transfer step at the mineral surface.

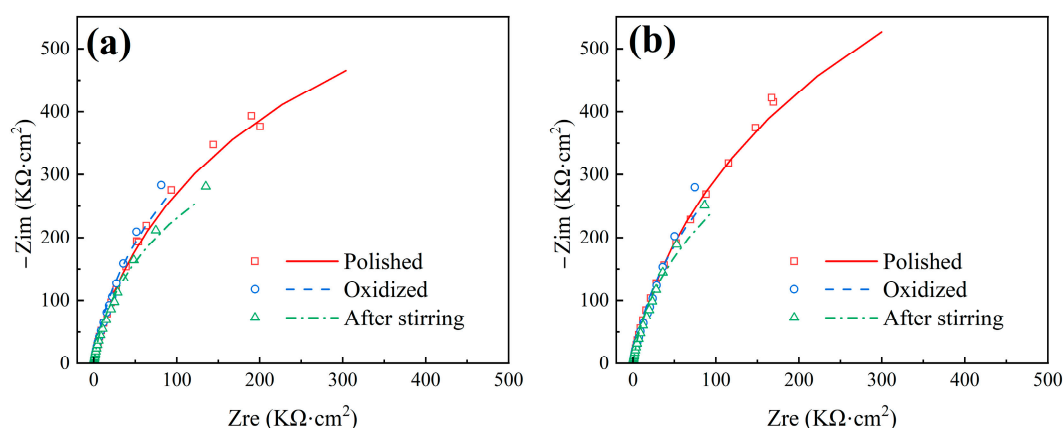


Figure 13. Nyquist diagram for chalcopryrite at different treatment stages (polished, oxidized, and after stirring). Symbols represent experimental data and solid lines represent fitted curves: (a) in quartz slurry; (b) in deionized water.

Based on the electrochemical impedance results, an equivalent circuit model was constructed as illustrated in Figure 14. In this model, R_s represents the solution resistance; R_{ct} denotes the charge-transfer resistance, which characterizes the kinetic resistance to charge transfer at the electrode/electrolyte interface; and the constant phase element (CPE) is

employed to simulate the interfacial capacitive behavior of non-ideal capacitors. The EIS data for chalcopyrite were fitted using ZView (V3.1) software, and the calculated parameters for each circuit element are summarized in Table 3.

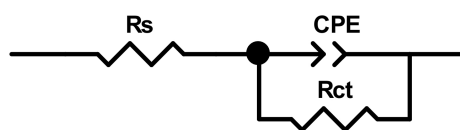


Figure 14. Equivalent electrical circuit models for EIS fitting.

Table 3. Equivalent circuit fitting parameters of chalcopyrite samples at different surface states (polished, oxidized, and after stirring).

Exp. No.	Surface States	R_s ($\Omega \cdot \text{cm}^2$)	Y_0 ($\mu\text{S} \cdot \text{s}^n \cdot \text{cm}^{-2}$)	n	R_{ct} ($\text{K}\Omega \cdot \text{cm}^2$)	χ^2 (10^{-3})
1	polished	36.75	19.50	0.92	1249	6.98
	oxidized	41.47	46.28	0.94	1209	5.62
	after stirring in quartz slurry	42.92	42.86	0.94	798	5.22
2	polished	44.09	18.23	0.92	1601	5.53
	oxidized	38.19	46.54	0.94	1218	6.70
	after stirring in deionized water	38.44	49.23	0.94	924	6.00

As indicated by the fitting results in Table 3, the differences in solution resistance (R_s) among the various sample groups are negligible, reflecting the consistency of the electrochemical environment during the measurements. The chi-square (χ^2) values are on the order of 10^{-3} , confirming an excellent goodness-of-fit between the proposed equivalent circuit model and the experimental EIS data. Furthermore, the exponent (n) of the constant phase element (CPE) consistently exceeds 0.9, indicating that the electrode interface exhibits near-ideal capacitive behavior and is minimally affected by surface roughness or heterogeneity.

In the two parallel experiments, electrochemical oxidation resulted in a significant elevation of the equivalent capacitance parameter (Y_0) for the chalcopyrite electrode, which increased from $19.50 \mu\text{S} \cdot \text{s}^n \cdot \text{cm}^{-2}$ and $18.23 \mu\text{S} \cdot \text{s}^n \cdot \text{cm}^{-2}$ to $46.28 \mu\text{S} \cdot \text{s}^n \cdot \text{cm}^{-2}$ and $46.54 \mu\text{S} \cdot \text{s}^n \cdot \text{cm}^{-2}$, respectively. Concurrently, the charge-transfer resistance (R_{ct}) exhibited a minor reduction, decreasing from $1249 \text{ K}\Omega \cdot \text{cm}^2$ and $1601 \text{ K}\Omega \cdot \text{cm}^2$ to $1209 \text{ K}\Omega \cdot \text{cm}^2$ and $1218 \text{ K}\Omega \cdot \text{cm}^2$. This transition is manifested in the Nyquist plots as a virtually constant capacitive loop radius accompanied by a markedly shortened arc length. Such a phenomenon indicates that the formed FeOOH overlayer imposes no significant barrier to the interfacial charge-transfer process; rather, its porous architecture expands the effective electrode/electrolyte contact area, thereby substantially enhancing the interfacial capacitance [28].

Following the stirring treatment in either the slurry or deionized water environment, the charge-transfer resistance (R_{ct}) of the oxidized chalcopyrite electrodes exhibited a notable decrease, dropping from $1209 \text{ K}\Omega \cdot \text{cm}^2$ and $1218 \text{ K}\Omega \cdot \text{cm}^2$ to $798 \text{ K}\Omega \cdot \text{cm}^2$ and $924 \text{ K}\Omega \cdot \text{cm}^2$, respectively. This trend is likely attributed to the dissolution of sulfoxy species within the oxide layer during the stirring and washing processes, which consequently reduces the resistance to interfacial charge transfer. However, the fluctuations in the equivalent capacitance parameter (Y_0) were confined to within 10%, falling well within the acceptable margin of experimental error. This indicates that the primary structure of the surface oxide layer did not undergo pronounced mechanical stripping under the influence of the hydrodynamic flow field.

Due to the random inter-particle collision mechanisms within turbulent slurry flows, dynamic discrepancies exist when compared to the “stationary specimen–flowing

particle” interaction mode employed in this study; consequently, the resulting mechanical stripping intensity may differ. To more authentically simulate the actual flotation process, the detachment behavior and evolution of oxidation products under complex hydrodynamic fields warrant further investigation.

3.8. Flotation of Actual Ore

Flotation tests were conducted on a copper ore sample from the Pulang copper deposit using both a conventional flowsheet and a combined collectorless pre-flotation–conventional flotation flowsheet, as shown in Figure 15. In the conventional flowsheet, MCO was used as the collector and lime as the depressant. In the collectorless pre-flotation flowsheet, an additional flotation stage with frother only was introduced upstream of the conventional circuit, and the concentrate from this stage was subjected to desliming flotation in the presence of a slime depressant to mitigate slime entrainment. The flotation results are summarized in Table 4.

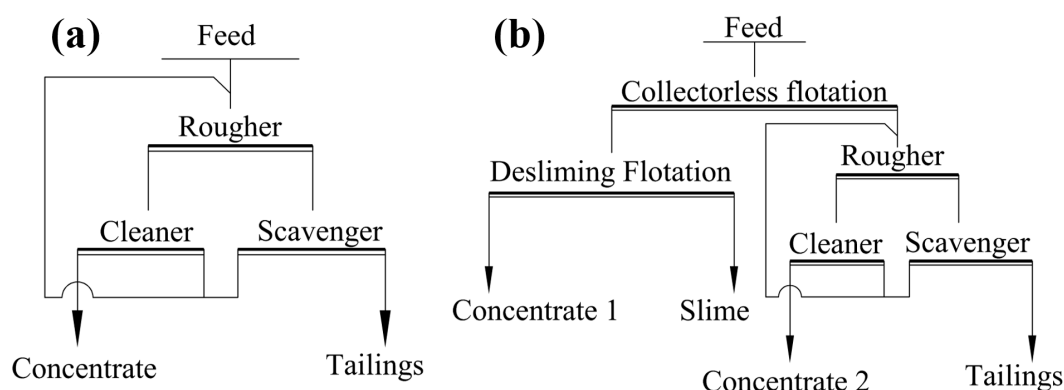


Figure 15. Flotation flowsheets for the conventional process (a) and for the process incorporating a collectorless pre-flotation stage (b).

Table 4. Flotation results for flowsheets with and without a collectorless pre-flotation stage.

Flotation Process	Product Designation	Yield (%)	Grade (%)	Recovery (%)
Conventional flotation	Concentrate	1.705	21.510	83.190
	Tailings	98.295	0.075	16.810
	Feed	100	0.441	100
Flotation with a collectorless pre-flotation stage	Concentrate 1	1.200	26.482	70.839
	Concentrate 2	0.412	17.930	16.483
	Slime	5.260	0.127	1.487
	Tailings	93.127	0.054	11.191
	Feed	100	0.449	100

Compared with the conventional process, the implementation of the pre-desliming flotation circuit improved the overall copper recovery (Concentrate 1 +Concentrate 2) from 83.19% to 87.32%, while the overall copper grade increased from 21.51% to 24.30%. These results correspond to absolute increases of 4.13 percentage points in recovery and 2.79 percentage points in copper grade.

The improved flotation performance observed in the collectorless pre-flotation circuit may be associated with the natural floatability of chalcopyrite and, potentially, with the removal of surface oxidation products through particle–particle interactions under turbulent conditions, as suggested by the fundamental studies presented above. However, owing to the complexity of the real ore system, the relative contributions of these mechanisms cannot be directly quantified in the present work.

Notably, more than 70% of the copper was recovered into the slime-bearing concentrate during the collectorless pre-flotation stage without the addition of collectors or pyrite depressants, indicating that a substantial proportion of chalcopyrite could be selectively recovered at an early stage. Furthermore, subsequent cleaning of this concentrate produced a relatively high-grade copper concentrate without requiring additional depressants.

From a process perspective, such a pre-flotation strategy may offer potential advantages by promoting early recovery of valuable minerals while reducing reagent consumption. In addition, the collectorless flotation stage removed a considerable fraction of fine slimes through entrainment, which may alleviate the adverse effects of slime coatings and competitive reagent adsorption in the subsequent conventional flotation stage, thereby contributing to improved flotation performance.

It should be noted, however, that these observations were obtained from laboratory-scale flotation tests on a specific ore sample. The flotation response of complex ores is influenced by numerous factors, including ore mineralogy, gangue characteristics, hydrodynamic conditions, water chemistry, and reagent schemes. Therefore, the results presented here should be regarded as a preliminary demonstration of the potential applicability of the concept rather than direct evidence that the mechanisms identified in the fundamental studies govern flotation behavior under practical operating conditions. Further studies are required to establish the relationship between the proposed mechanisms and flotation performance in more complex systems.

4. Conclusions

This study systematically elucidates the mechanisms underlying the influence of quartz on the flotation behavior of chalcopyrite in a collectorless flotation system through micro-flotation experiments, surface analysis techniques, and electrochemical oxidation simulations. The results indicate that the incorporation of quartz significantly enhances the recovery of chalcopyrite, and this promoting effect becomes more pronounced with increasing degrees of chalcopyrite oxidation and larger quartz particle sizes. Microscopic particle size analysis corroborates that the addition of quartz primarily facilitates the recovery of the relatively coarser chalcopyrite particles. Furthermore, XPS analysis demonstrates that quartz particles effectively remove the hydrophilic iron (oxy)hydroxide species from the chalcopyrite surface during the stirring process, with coarser quartz particles exhibiting a higher degree of removal. Collectively, these experimental findings demonstrate that this promoting effect exhibits a pronounced particle size dependency.

To gain deeper insights into the underlying mechanisms, this study employed electrochemical techniques to construct a simulated iron (oxy)hydroxide layer on the chalcopyrite surface. The results of mechanical scratch, contact angle, and electrochemical impedance spectroscopy (EIS) measurements reveal that this oxide layer possesses a loose and porous structure, exhibits profound hydrophilicity, and displays weak interfacial adhesion to the underlying mineral substrate. These micro-interfacial characteristics further substantiate the “surface scrubbing” mechanism exerted by quartz on chalcopyrite.

To explore the potential practical implications of the findings obtained in this study, a combined collectorless pre-flotation–conventional flotation flowsheet was tested using an actual copper ore from the Pulang copper deposit in Yunnan. Compared with the conventional flowsheet, the new flowsheet increased the Cu grade of the concentrate by 2.79% and the Cu recovery by 4.13%, while reducing overall reagent consumption. These results demonstrate the potential of the proposed approach, although further studies are required to assess its applicability under more representative operating conditions.

This study suggests that the presence of quartz can enhance the floatability of chalcopyrite, possibly through the removal of ferric oxyhydroxide species from the

chalcopyrite surface during particle–particle interactions. These findings provide insights into the potential application of collectorless pre-flotation technology for copper ore processing.

Author Contributions: Conceptualization, methodology, writing—original draft preparation, L.S.; writing—review and editing, F.J.; investigation, validation, data curation, formal analysis, D.L., Y.C. and X.W.; supervision, M.A.; project administration, W.S.; funding acquisition, L.S. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Key Research and Development Program of China (grant No. 2023YFC3904202) and the National Science and Technology Major Project of China (grant No. 2024ZD1004004).

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author(s).

Acknowledgments: The authors thank the above funding for supporting this project. The authors also thank the contributions of reviewers for this manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

To evaluate whether the Cu grades measured by XRF can reflect the relative variation in Cu content, a series of quartz–chalcopyrite mixtures with different chalcopyrite proportions were prepared and analyzed by XRF. The relationship between the chalcopyrite proportion in the synthetic mineral mixtures and the Cu grade measured by XRF is shown in Figure A1.

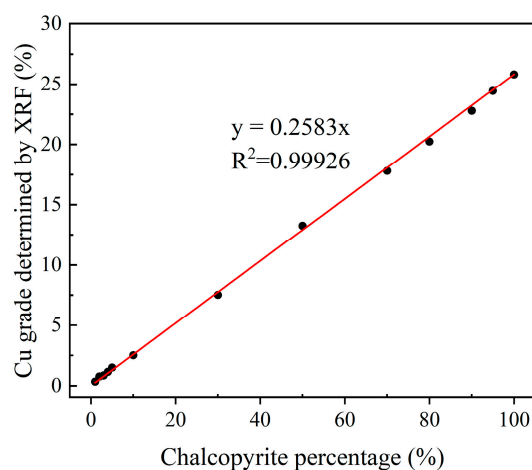


Figure A1. Relationship between chalcopyrite proportion and Cu grade determined by XRF.

As shown in Figure A1, the XRF-measured Cu grades exhibit a strong linear relationship with the chalcopyrite proportion over the investigated range. This result indicates that although the absolute Cu grades obtained by XRF may differ from the actual values, the measured XRF values maintain a proportional relationship with the chalcopyrite content in the synthetic mixtures. Therefore, the XRF results are suitable for reflecting relative changes in Cu grade and can be used for calculating and comparing flotation recoveries in the present study.

References

1. Yu, X.; Zhang, R.; Zeng, Y.; Cheng, C.; Huang, Z.; Wang, J.; He, G.; Wang, H. The Effect and Mechanism of Cinnamic Hydroxamic Acid as a Collector in Flotation Separation of Malachite and Calcite. *Miner. Eng.* **2021**, *164*, 106847. <https://doi.org/10.1016/j.mineng.2021.106847>.
2. Zhang, Q.; Wen, S.; Feng, Q.; Zhang, S. Surface Characterization of Azurite Modified with Sodium Sulfide and Its Response to Flotation Mechanism. *Sep. Purif. Technol.* **2020**, *242*, 116760. <https://doi.org/10.1016/j.seppur.2020.116760>.
3. Chen, L.; Xiong, T.; Xiong, D.; Yang, R.; Peng, Y.; Shao, Y.; Xu, J.; Zeng, J. Pulsating HGMS for Industrial Separation of Chalcopryrite from Fine Copper-Molybdenum Co-Flotation Concentrate. *Miner. Eng.* **2021**, *170*, 106967. <https://doi.org/10.1016/j.mineng.2021.106967>.
4. Chen, J.; Wang, J.; Li, Y.; Liu, M.; Liu, Y.; Zhao, C.; Cui, W. Effects of Surface Spatial Structures and Electronic Properties of Chalcopryrite and Pyrite on Z-200 Selectivity. *Miner. Eng.* **2021**, *163*, 106803. <https://doi.org/10.1016/j.mineng.2021.106803>.
5. Hu, J.; Zhou, S.; Liao, S.; Gu, G.; Wang, Y. Effect of Oxidized Pyrite Activating Persulfate on the Degradation of Aniline Aero-float: Mechanism and Degradation Pathway. *Miner. Eng.* **2023**, *201*, 108233. <https://doi.org/10.1016/j.mineng.2023.108233>.
6. Liu, S.; Xie, L.; Liu, G.; Zhong, H.; Wang, Y.; Zeng, H. Hetero-Difunctional Reagent with Superior Flotation Performance to Chalcopryrite and the Associated Surface Interaction Mechanism. *Langmuir* **2019**, *35*, 4353–4363. <https://doi.org/10.1021/acs.langmuir.9b00156>.
7. Park, I.; Hong, S.; Jeon, S.; Ito, M.; Hiroyoshi, N. A Review of Recent Advances in Depression Techniques for Flotation Separation of Cu–Mo Sulfides in Porphyry Copper Deposits. *Metals* **2020**, *10*, 1269. <https://doi.org/10.3390/met10091269>.
8. Zhu, H.; Ke, B.; Lei, L.; Feng, H.; Wan, J.; Shen, Z. Influence of Galvanic Interaction between the Iron Grinding Medium and Chalcopryrite on Collectorless Flotation Behavior of Chalcopryrite: Experimental and Density Functional Theory Study. *Langmuir* **2024**, *40*, 462–473. <https://doi.org/10.1021/acs.langmuir.3c02720>.
9. Lin, S.; Liu, R.; Hu, Y.; Sun, W.; Shi, Z.; Han, H.; Li, W. Optimize Flotation Process of Mo–Bi Sulfide Ore for Cleaner Production. *J. Clean. Prod.* **2021**, *291*, 125236. <https://doi.org/10.1016/j.jclepro.2020.125236>.
10. Gardner, J.R.; Woods, R. An Electrochemical Investigation of the Natural Flotability of Chalcopryrite. *Int. J. Miner. Process.* **1979**, *6*, 1–16. [https://doi.org/10.1016/0301-7516\(79\)90028-0](https://doi.org/10.1016/0301-7516(79)90028-0).
11. Hu, Y.; Sun, W.; Wang, D. *Electrochemistry of Flotation of Sulphide Minerals*; Springer: Berlin/Heidelberg, Germany, 2010; p. 30.
12. Buckley, A.; Woods, R. An X-Ray Photoelectron Spectroscopic Study of the Oxidation of Chalcopryrite. *Aust. J. Chem.* **1984**, *37*, 2403. <https://doi.org/10.1071/CH9842403>.
13. Hornn, V.; Park, I.; Ito, M.; Shimada, H.; Suto, T.; Tabelin, C.B.; Jeon, S.; Hiroyoshi, N. Agglomeration-Flotation of Finely Ground Chalcopryrite Using Surfactant-Stabilized Oil Emulsions: Effects of Co-Existing Minerals and Ions. *Miner. Eng.* **2021**, *171*, 107076. <https://doi.org/10.1016/j.mineng.2021.107076>.
14. Zeng, Q.; Feng, X.; Ren, H.; Sui, S.; Wang, S.; Sun, W.; Liu, J. The Impact of New Composite Curing Agents on the Curing Properties of Glacial Debris in the Pulang Copper Deposit. *Buildings* **2023**, *13*, 2189. <https://doi.org/10.3390/buildings13092189>.
15. Gong, J.; Peng, Y.; Bouajila, A.; Ourriban, M.; Yeung, A.; Liu, Q. Reducing Quartz Gangue Entrainment in Sulphide Ore Flotation by High Molecular Weight Polyethylene Oxide. *Int. J. Miner. Process.* **2010**, *97*, 44–51. <https://doi.org/10.1016/j.minpro.2010.07.009>.
16. Wang, M.; Zhang, G.; Chen, Y.; Zhao, L. Effect of Surface Oxidization on Quartz Slime Coating in the Sulfidization-Amine Flotation of Smithsonite. *Miner. Eng.* **2022**, *188*, 107847. <https://doi.org/10.1016/j.mineng.2022.107847>.
17. Qin, W.; Wu, J.; Jiao, F. Mechanism of Different Particle Sizes of Quartz Activated by Metallic Ion in Butyl Xanthate Solution. *J. Cent. South Univ.* **2017**, *24*, 56–61. <https://doi.org/10.1007/s11771-017-3408-x>.
18. Biesinger, M.C. Advanced Analysis of Copper X-ray Photoelectron Spectra. *Surf. Interface Anal.* **2017**, *49*, 1325–1334. <https://doi.org/10.1002/sia.6239>.
19. Li, Y.; Kawashima, N.; Li, J.; Chandra, A.P.; Gerson, A.R. A Review of the Structure, and Fundamental Mechanisms and Kinetics of the Leaching of Chalcopryrite. *Adv. Colloid Interface Sci.* **2013**, *197–198*, 1–32. <https://doi.org/10.1016/j.cis.2013.03.004>.
20. Harmer, S.L.; Thomas, J.E.; Fornasiero, D.; Gerson, A.R. The Evolution of Surface Layers Formed during Chalcopryrite Leaching. *Geochim. Cosmochim. Acta* **2006**, *70*, 4392–4402. <https://doi.org/10.1016/j.gca.2006.06.1555>.
21. Tehrani, M.E.H.N.; Naderi, H.; Rashchi, F. Electrochemical Study and XPS Analysis of Chalcopryrite Dissolution in Sulfuric Acid in the Presence of Ethylene Glycol. *Electrochim. Acta* **2021**, *369*, 137663. <https://doi.org/10.1016/j.electacta.2020.137663>.
22. Ghahremaninezhad, A.; Dixon, D.G.; Asselin, E. Electrochemical and XPS Analysis of Chalcopryrite (CuFeS₂) Dissolution in Sulfuric Acid Solution. *Electrochim. Acta* **2013**, *87*, 97–112. <https://doi.org/10.1016/j.electacta.2012.07.119>.

23. Yang, X.; Li, Y.; Fan, R.; Duan, W.; Huang, L.; Xiao, Q. Separation Mechanism of Chalcopyrite and Pyrite Due to H₂O₂ Treatment in Low-Alkaline Seawater Flotation System. *Miner. Eng.* **2022**, *176*, 107356. <https://doi.org/10.1016/j.mineng.2021.107356>.
24. Brion, D. Etude par spectroscopie de photoelectrons de la degradation superficielle de FeS₂, CuFeS₂, ZnS et PbS a l'air et dans l'eau. *Appl. Surf. Sci.* **1980**, *5*, 133–152. [https://doi.org/10.1016/0378-5963\(80\)90148-8](https://doi.org/10.1016/0378-5963(80)90148-8).
25. Velásquez, P.; Leinen, D.; Pascual, J.; Ramos-Barrado, J.R.; Grez, P.; Gómez, H.; Schrebler, R.; Del Río, R.; Córdova, R. A Chemical, Morphological, and Electrochemical (XPS, SEM/EDX, CV, and EIS) Analysis of Electrochemically Modified Electrode Surfaces of Natural Chalcopyrite (CuFeS₂) and Pyrite (FeS₂) in Alkaline Solutions. *J. Phys. Chem. B* **2005**, *109*, 4977–4988. <https://doi.org/10.1021/jp048273u>.
26. Farquhar, M.L.; Wincott, P.L.; Wogelius, R.A.; Vaughan, D.J. Electrochemical Oxidation of the Chalcopyrite Surface: An XPS and AFM Study in Solution at pH 4. *Appl. Surf. Sci.* **2003**, *218*, 34–43. [https://doi.org/10.1016/S0169-4332\(03\)00538-5](https://doi.org/10.1016/S0169-4332(03)00538-5).
27. Hassanzadeh, A.; Gholami, H.; Özkan, S.G.; Niedoba, T.; Surowiak, A. Effect of Power Ultrasound on Wettability and Collector-Less Floatability of Chalcopyrite, Pyrite and Quartz. *Minerals* **2021**, *11*, 48. <https://doi.org/10.3390/min11010048>.
28. Simon, P.; Gogotsi, Y. Materials for Electrochemical Capacitors. *Nat. Mater.* **2008**, *7*, 845–854. <https://doi.org/10.1038/nmat2297>.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.