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Enhanced sulfidization flotation of cuprite by surface modification with hydrogen peroxide

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Abstract: Hydrogen peroxide was used as an oxidant to modify the cuprite surface and enhance its sulfidization. Surface-adsorption and infrared spectroscopy measurements indicated that the modification of the cuprite surface with hydrogen peroxide before sulfidization increased the adsorption capacity of xanthate. Zeta potential, scanning electron microscopy-energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and time-of-flight secondary ion mass spectrometry results showed that the modification with hydrogen peroxide increased the contents of S²⁻ and S²⁻_n species on the cuprite surface. Microflotation tests showed that the recovery of cuprite increased from 61.74% to 83.30% after the modification of the surface with hydrogen peroxide. These results confirm that the modification of the cuprite surface is floation. **Key words:** cuprite; floation; hydrogen peroxide; surface modification; sulfidization

1 Introduction

Among more than 280 kinds of copper-bearing minerals that have been discovered in the world, the copper minerals with industrial value are chalcopyrite, chalcocite, malachite, cuprite, and azurite [1-5]. Copper sulfide ore resources have diminished in recent years, which attracted much attention. Sulfidization flotation is widely used in mineral processing to recover copper oxide ore resources [6,7]. Among the sulfidization flotation methods, surface sulfidization is the most commonly used, economical, and mature process for the treatment of common copper oxide ore resources. Sulfidization flotation is performed by treating copper oxide minerals with a sulfurizing reagent, which is usually sodium sulfide, for pre-sulfidization. This generates a metal sulfide film with improved hydrophobicity on the mineral surface. The sulfide ore is then collected by flotation [8,9].

Many factors affect the sulfidization behavior of oxide minerals, and in turn the flotation. These factors include the pulp temperature, pulp pH, dose and addition method of the sulfurizing reagent, and mineral characteristics, and there may be interactions among these factors [10-12]. An increase in the temperature can improve the reaction rate and degree of sulfidization. Hydrothermal sulfidization uses a high temperature and high pressure to obtain a higher rate of sulfidization and convert all the oxide ores into sulfide [13]. However, industrial applications of hydrothermal sulfidization are limited because of its high setup costs and energy consumption.

The pulp pH can affect the forms of the flotation reagents and mineral surface properties in the pulp. Because of the hydrolytic equilibrium of sodium sulfide in aqueous solution, the form of

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sodium sulfide in the pulp is controlled by the pH. The dominant components at pH<7, 7<pH<13.9, and pH>13.9 are H₂S, HS⁻, and S²⁻, respectively. Previous research has shown that oxide minerals have better flotation indexes in weakly alkaline pulp than at other pH values, and the dominant sodium sulfide component in this pH range is HS⁻ [14]. The sodium sulfide dose is the most important factor affecting the sulfidization flotation of oxide minerals, with both insufficient and excessive doses not conducive to flotation [15]. With insufficient sodium sulfide, the area of sulfide products on oxide mineral surfaces is not enough to activate flotation of the minerals. With an excess of sodium sulfide, flotation of the minerals is depressed. Although the surface sulfidization has some deficiencies, such as the required dose of sulfurizing reagent, low sulfidization efficiency, high collector dose, and low metal recovery, it is still the most economical and promising process for the flotation of oxide minerals because of its low setup costs and energy consumption. To improve the sulfidization flotation of oxide minerals, surface enhancement has been applied. Previous studies have shown that the addition of a certain amount of activation reagent (e.g., ammonium sulfate or ethylenediamine) can enhance the sulfidization of copper oxide minerals. This decreases the required dose of sulfurizing reagent and greatly enhances the hydrophobicity of the minerals to improve the flotation recovery [16,17].

Cuprite is an important copper oxide mineral for copper extraction. Because of a lack of oxygen in the mineralization process, copper is not oxidized sufficiently and forms cuprous minerals. The surface of cuprite is strongly hydrophilic, therefore, flotation with direct sulfidization is not ideal [18]. In previous work, the flotation recovery of cuprite for a mixed oxide-sulfide copper ore containing cuprite was significantly increased by modification with an oxidant [19]. However, the affecting mechanism of modification by the oxidant on the surface properties and sulfidization of cuprite is not clear. In this work, hydrogen peroxide (H₂O₂) was used as an oxidant to modify the cuprite surface and improve its subsequent sulfidization. The modified and sulfidized cuprite surfaces were characterized and the influence of H₂O₂ on sulfidization of the cuprite surface and xanthate adsorption was

evaluated. The aim of this work was to investigate the use of H_2O_2 as an oxidant to modify the cuprite surface and enhance sulfidization. The results of this study will be beneficial to copper oxide sulfidization flotation.

2 Experimental

2.1 Materials

Cuprite samples were collected in Yunnan Province, China. The cuprite blocks were crushed and purified by hand separation. The cuprite surface was then rinsed repeatedly with deionized water. After removing the surface water, an agate grinding machine was used for preliminary grinding of the cuprite samples. A standard sieve was used to screen the cuprite samples to meet the sample size requirements for different tests. The cuprite samples were stored in sealed glass bottles. To determine the purity of the cuprite samples, X-ray diffraction and chemical analyses were performed. The results are shown in Fig. 1 and Table 1. The diffraction peaks of the cuprite sample were consistent with the standard diffraction peaks, and no obvious impurity peaks were observed. The impurity contents of the cuprite samples were very low (Table 1). According to the Cu content (84.43 wt.%), the sample purity was about 95%. The X-ray diffraction and chemical analyses results showed that the cuprite sample purity met the requirements for single mineral tests.



Fig. 1 X-ray diffraction pattern of cuprite sample

 Table 1 Main chemical composition of cuprite sample (wt.%)

Cu	Fe	SiO ₂	Al ₂ O ₃	CaO	MgO
84.43	0.17	0.5	0.25	0.01	0.01

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2.2 Reagents

 H_2O_2 (Chongqing Maoye Chemical Co., Ltd., China) was used as an oxidant for cuprite. $Na_2S \cdot 9H_2O$ (Sinopharm Chemical Reagent Co., Ltd., China) was used for sulfidization. Sodium butyl xanthate (NaBX; Zhuzhou Flotation Reagents Co., Ltd., China) was used as a collector. HCl and NaOH were used as pH regulators. All reagents were of analytical grade, except for NaBX, which was of industrial grade.

2.3 SEM-EDS measurements

The surface morphologies and energy spectra of cuprite samples were measured using a scanning electron microscope (FEI Quanta 200, FEI Company, USA) and an energy dispersive spectrometer (Genesis 2000, EDAX Company, USA). The particle size of the cuprite was between 45 and 74 µm, and the sample mass for each test was 0.5 g. The modification with H_2O_2 was performed at a natural pH, and the pulp pH was adjusted to 9.5 during the sulfidization process. Each cuprite sample was placed in a beaker and a H_2O_2 solution was added with stirring for 5 min. Then, the prepared Na₂S solution was added with stirring for 30 min. A solution of HCl or NaOH was also added to adjust the pH during the sulfidization process. Finally, the samples were dried and used for SEM-EDS measurements.

2.4 Zeta potential tests

Zeta potential tests were performed using a zeta analyzer (Zetasizer–3000HS, Malvern Panalytical, United Kingdom). Cuprite samples with a particle size less than 2 μ m were used in the tests. A planetary ball mill (RETSCH-MM400, Verder Shanghai Instruments and Equipment Ltd.) was used to obtain particles with sizes less than 2 μ m. The particle size was determined using a granulometer (BT–9300S, Bettersize Instruments Ltd., China). Each sample was weighed to 0.05 g and transferred to a 100-mL beaker. A certain volume of KCl solution was added and the pulp was stirred. The same reagents used for the SEM-EDS measurements were added successively, with each reagent allowed to react for a certain time.

2.5 XPS measurements

The X-ray photoelectron spectroscopy (XPS)

measurements were carried out with a PHI 5000 VersaProbe II instrument (PHI 5000, ULVAC-PHI, Japan) using an Al K_{α} X-ray source under ultrahigh vacuum. The operating conditions were as follows: pass energy of 46.95 eV, step size of 0.2 eV, power of 50 W, and voltage of 15 kV. The cuprite samples (particle size <38 μ m, sample mass of 0.5 g) were weighed and the same reagents used for the SEM-EDS measurements (Section 2.3) were added successively.

2.6 Surface adsorption tests

Surface adsorption tests were conducted using an ultraviolet-visible spectrophotometer (UV-2700, Shimadzu, Japan). Cuprite samples (particle size <38 μ m) were weighed (0.5 g) and treated with the same reagents as for the SEM-EDS measurements.

2.7 Infrared spectroscopy measurements

Infrared (IR) spectroscopy was performed using a Fourier-transform IR spectrometer (Nicolet iS50, Thermo Fisher Scientific, USA). The wavenumber range was 400–4000 cm⁻¹. The cuprite sample (particle size $<38 \ \mu m$) was weighed (0.5 g) and treated with the same reagents as for the SEM-EDS measurements.

2.8 Time-of-flight secondary ion mass spectrometry measurements

The chemical properties of the cuprite surface were characterized using time-of-flight secondary ion mass spectrometry (ToF-SIMS; ION-TOF IV, IONTOF, Munster, Germany). High-purity cuprite was manually selected for cutting. Before analysis, the cuprite sample was cleaned in ethanol using ultrasonication. The sample was then placed in a beaker and treated with the same reagents as for the SEM-EDS measurements.

2.9 Microflotation tests

Flotation tests of cuprite were carried out using a Hallimond tube, the effective volume was 50 mL, and N₂ was used as the gas source (20 mL/min). Cuprite samples (0.5 g) with a particle size between 45 and 74 μ m were used as the flotation feed. Each cuprite sample was treated with reagents before flotation. A solution of H₂O₂ was added to the pulp and stirred for 5 min. Then, the prepared Na₂S solution was added and stirred for 3 min, and a solution of HCl or NaOH was added to adjust the pH for the sulfidization process. The collector (NaBX) was added with stirring for 3 min. Finally, the Hallimond tube was used to float the mixture for 3 min. The tailings and concentrate were collected, dried, and weighed to calculate the flotation recovery. Each group of flotation tests was performed three times, and the final results were averaged.

3 Results and discussion

3.1 Effect of H₂O₂ on surface properties of cuprite

3.1.1 Surface morphology and zeta potential

SEM can be used to observe the morphologies of localized mineral surfaces to determine changes in the morphology before and after treatment with different reagents [20,21]. We investigated the surface morphology and zeta potential of blank cuprite and H₂O₂-treated cuprite to study the influence of H₂O₂ on the surface properties of cuprite. Secondary electron images of cuprite surfaces with and without H₂O₂ treatment are shown in Fig. 2. The surface of the cuprite without H_2O_2 treatment was smooth (Fig. 2(a)). After treatment with H_2O_2 , the cuprite surface became rough and multiple cracks appeared (Fig. 2(b)). This increased the specific surface area of the cuprite particles, which would facilitate subsequent adsorption of sulfur ions. The zeta potential of cuprite was measured in the absence and presence of 5×10^{-4} mol/L H₂O₂ at different pH values (Fig. 3). In the investigated pH range (6.5-11.5), the zeta potential of H2O2-treated cuprite was obviously lower than that of blank cuprite (Fig. 3). This indicated that the treatment of cuprite with H₂O₂ modified its surface characteristics, which changed the surface potential.

3.1.2 XPS spectra

The elements on the surface of a sample and their chemical environments can be determined by XPS using the binding energies of different elements. Semi-quantitative results for the content of each element can be obtained using the area of the spectral line [22–26]. We conducted XPS measurements for cuprite with and without modification to confirm the influence of H_2O_2 on the cuprite surface properties. In the O 1s spectra of cuprite with and without modification (Fig. 4), a peak at approximately 530.11 eV was assigned to



Fig. 2 Secondary electron images of cuprite surfaces at pH 9.5: (a) Untreated; (b) Treated with 5×10^{-3} mol/L H₂O₂



Fig. 3 Zeta potential of cuprite as function of pH in the absence and presence of 5×10^{-4} mol/L H₂O₂

O(II) species from cuprite, and a higher intensity peak at approximately 531.62 eV was assigned to O(II) species from compounds containing hydroxyl groups on the cuprite surface [27,28]. After treatment with H₂O₂, the binding energies and distribution of the O(II) species from compounds containing hydroxyl groups and cuprite did not change significantly. This indicated that the chemical state of the O(II) species on cuprite was relatively stable regardless of the addition of H₂O₂. 3568

In the Cu 2p spectra of cuprite with and without modification (Fig. 5), a peak at approximately 934.57 eV was assigned to Cu(II) species on the cuprite surface, and a peak at approximately 932.98 eV was assigned to Cu(I) species [29]. There were no large shifts in the binding energies for copper species on cuprite after treatment with H_2O_2 . However, the proportion of Cu(II) species on the cuprite surface increased significantly, and this change may enhance the adsorption of sulfur ions on cuprite. Figure 6 shows the molar fractions of Cu(I) and Cu(II) species on



Fig. 4 O 1s XPS spectra of cuprite surfaces: (a) Untreated; (b) Treated with 5×10^{-4} mol/L H₂O₂



Fig. 5 Cu 2p XPS spectra of cuprite surfaces: (a) Untreated; (b) Treated with 5×10^{-4} mol/L H₂O₂

the cuprite surfaces with and without modification. After treatment with H₂O₂, the molar fraction of Cu(I) species decreased from 11.67% to 7.46%, and that of Cu(II) species increased from 10.32% to 12.43%. These results indicated that more Cu(II) species were generated on cuprite, which could interact with sulfur ions and be reduced to Cu(I). Table 2 shows the proportions of Cu(I) and Cu(II) species among the total copper species on the cuprite surfaces with and without modification. The proportion of Cu(II) species among the total copper species increased from 46.92% to 62.51% and the proportion of Cu(I) species decreased from 53.08% to 37.49%. This indicated that some of the Cu(I) species on the cuprite surface were oxidized to Cu(II) species after addition of H₂O₂. Compared with Cu(I) species, the newly generated Cu(II) species had a superior ability to interact with sulfur ions in the pulp through oxidation-reduction reactions. This implied that the modification of the cuprite surface strengthened the sulfidization process of cuprite. Therefore, we inferred that modification using H₂O₂ before sulfidization could transform Cu(I) species on cuprite surfaces to Cu(II) species, which would enhance the adsorption of sulfur ions.



Fig. 6 Molar fractions of copper species on blank cuprite surface and H_2O_2 -treated cuprite surface

Table 2 Quantification of Cu 2p species on cuprite surfaces untreated and treated with 5×10^{-4} mol/L H₂O₂

Sample	Species	$Cu\ 2p_{3/2}\ binding$	Species
		energy/eV	proportion/%
Untreated	Cu(I)	932.98	53.08
	Cu(II)	934.57	46.92
Treated with H ₂ O ₂	Cu(I)	932.95	37.49
	Cu(II)	934.58	62.51

3.2 Effect of modification on sulfidization of cuprite and xanthate adsorption

3.2.1 Surface-adsorption behavior

Xanthate (NaBX) can be ionized in aqueous solution to produce anions containing sulfur atoms, which can interact with the mineral surface. This interaction forms a metal xanthate that is firmly connected to the interior of the crystal lattice. In this way, xanthate is fixed on the mineral surface, so it can play a role in collection. The amount of xanthate adsorbed on cuprite surfaces is critical in determining the hydrophobicity of cuprite. Therefore, to study the impact of modification on the adsorption of NaBX, we investigated the quantity of NaBX adsorbed on cuprite surfaces with changes in the H₂O₂ and NaBX concentrations. The Na₂S concentration was set to be 1×10^{-3} mol/L and the pH to be 9.5 (Fig. 7). The consumption of NaBX was significantly higher with H₂O₂ modification than without modification (Fig. 7(a)). This result indicated that modification with H₂O₂



Fig. 7 Quantity of NaBX adsorbed on cuprite surface as function of H_2O_2 concentration (a) and NaBX concentration (b) at 1×10^{-3} mol/L Na₂S and pH 9.5

before sulfidization could enhance the adsorption capacity of cuprite surfaces for NaBX. Higher consumption of NaBX on modified cuprite compared with unmodified cuprite was observed for all the investigated NaBX concentrations (Fig. 7(b)). This result also indicated that with the same collector dose, modification using H₂O₂ could increase the amount of collector adsorbed on the cuprite surface. This could reduce the collector dose required for use in industrial production. A decrease in collector consumption could enhance the selectivity of the collector during the flotation process and improve the flotation pulp environment. The surface-adsorption results indicated that modification with H₂O₂ before sulfidization increased the amount of NaBX adsorbed on the cuprite surface. This would improve the hydrophobicity of the cuprite surface and enhance the floatability.

3.2.2 IR spectra

IR spectroscopy was used to investigate the effect of modification on the adsorption of NaBX on sulfide-treated cuprite by analyzing specific peaks for the mineral and reagents in the spectra [30,31]. The peaks observed for cuprite and NaBX (Fig. 8) were consistent with those in Refs. [32,33]. In the IR spectrum of NaBX, peaks at 1190 and 1167 cm⁻¹ were assigned to the C—O—C asymmetric stretching vibration. Peaks at 1108 and 1063 cm⁻¹ were attributed to the C—O—C symmetric stretching vibration and C—S stretching vibration, respectively. After treatment with NaBX,



Fig. 8 IR spectra of NaBX, cuprite, cuprite treated with Na₂S and NaBX, and cuprite treated with H_2O_2 , Na₂S, and NaBX at pH 9.5

a new peak appeared at 1202 cm^{-1} in the IR spectrum of the directly sulfidized cuprite surface. This could be attributed to a shift in the C—O—C asymmetric stretching vibration for NaBX from 1190 to 1202 cm⁻¹ after its interaction with cuprite surfaces. For the cuprite treated with H₂O₂, Na₂S, and NaBX, the C-O-C asymmetric stretching vibration peak at 1201 cm⁻¹ in the IR spectrum increased in intensity. This result showed that NaBX could interact with cuprite surface more strongly after it was modified. These results were consistent with the results of the surface-adsorption measurements. Therefore, the hydrophobicity of the cuprite surface could be enhanced by modification with H₂O₂ before sulfidization of cuprite, and this change would considerably improve the cuprite flotation.

3.2.3 Zeta potential

Sulfur ions in the pulp can shield the charge on the cuprite surface by interacting with copper sites, which will change the electrical properties of the cuprite surface. Our earlier results suggested that modification with H₂O₂ could improve the floatability of cuprite by enhancing the adsorption of Na₂S on cuprite surfaces. Next, we studied the effect of modification on the sulfidization of cuprite by measuring the zeta potentials of cuprite surfaces. The zeta potentials of cuprite surfaces were measured in the absence and presence of $\mathrm{H_2O_2}$ at different pH values. The NaBX concentration was set to be 5×10^{-4} mol/L (Fig. 9). In the investigated pH range (6.5-11.5), the zeta potential of the oxidant- and sulfide-treated cuprite was obviously lower than that of sulfide-treated cuprite (Fig. 9). This result indicated that modification increased the adsorption of sulfur ions on the cuprite surface. Therefore, H₂O₂ and Na₂S in cuprite flotation had a positive synergistic effect on the adsorption of sulfur ions on cuprite, which could improve its hydrophobicity. The zeta potential results proved that modification using H₂O₂ before sulfidization could enhance the adsorption of sulfur ions on cuprite. This would provide favorable conditions for the subsequent interaction of NaBX with the cuprite surface.

3.2.4 SEM-EDS images

SEM-EDS can be used for the qualitative and semi-quantitative analysis of localized cuprite surfaces [34,35]. We performed SEM-EDS analysis to support the zeta potential results and investigate



Fig. 9 Zeta potential of sulfide-treated cuprite as function of pH in the absence and presence of H_2O_2 at 1×10^{-3} mol/L Na₂S

the effect of modification on the sulfidization of cuprite. Secondary electron images and EDS results were obtained for the sulfide-treated cuprite surfaces with and without modification (Fig. 10). Copper sulfide particles appeared in some areas on the cuprite surface (Fig. 10(a)). These particles were produced by sulfur ions interacting with copper sites on cuprite surface. Compared with sulfide-treated cuprite surfaces without the modification, there were more copper sulfide particles on the oxidant- and sulfide-treated cuprite surfaces (Fig. 10(b)). The molar fractions of sulfur in these areas increased from 8.69% to 21.10% compared with the non-modified cuprite. This increase indicated that the cuprite surface treated with H₂O₂ could interact better with sulfur ions than the untreated surface. This meant that more sulfide species could be generated on the cuprite surface. The SEM-EDS further proved that modification with H₂O₂ could enhance the sulfidization of cuprite, which would promote subsequent xanthate adsorption on the mineral surface.

3.2.5 ToF-SIMS images

ToF-SIMS images of selected ions for the sulfide-treated cuprite surfaces without and with modification are shown in Figs. 11 and 12, respectively. The normalized intensities of the secondary ions on the sulfide-treated cuprite surfaces with and without modification are shown in Fig. 13. The ions selectively detected in the secondary ion images of the sulfide-treated cuprite surface and sulfide-treated cuprite surface with modification were CuS⁺ (m/z=94.895),



Fig. 10 Secondary electron images and EDS results for cuprite surfaces at pH 9.5: (a) Treated with 5×10^{-3} mol/L Na₂S; (b) Treated with 5×10^{-3} mol/L H₂O₂ and 5×10^{-3} mol/L Na₂S



Fig. 11 ToF-SIMS images of selected ions for Na₂S-treated cuprite surface obtained in surface imaging operational mode: (a) CuS⁺; (b) S⁻; (c) S⁻₂; (d) S⁻₃



Fig. 12 ToF-SIMS images of selected ions for H₂O₂- and Na₂S-treated cuprite surface obtained in surface imaging operational mode: (a) CuS⁺; (b) S⁻; (c) S⁻₂; (d) S⁻₃



Fig. 13 Normalized intensities of secondary ions on Na₂S-treated cuprite surfaces with and without modification

 $S^{-}(m/z=31.973)$, $S_{2}^{-}(m/z=63.945)$, and $S_{3}^{-}(m/z=95.921)$. The normalized intensities of CuS⁺, S⁻, S₂⁻, and S₃⁻ were greatly enhanced on sulfide-treated cuprite surface with modification compared with that without modification. This indicated that the modification using H₂O₂ could strengthen the

adsorption of Na_2S on cuprite. In addition, the ToF-SIMS results confirmed that the normalized intensities of the copper sulfide species and polysulfide species on cuprite increased after treatment with H_2O_2 , which improved the hydrophobicity of the cuprite surface. These results supported the zeta potential and SEM-EDS results. 3.2.6 XPS spectra

Modification with H_2O_2 could enhance the sulfidization of cuprite and increase the adsorption of NaBX on the cuprite surface. We performed XPS analysis of sulfide-treated cuprite surfaces with and without modification to confirm the influence of modification on sulfidization of cuprite. The results were used to study the properties of sulfidization products on cuprite surfaces with and without modification and to identify the mechanism of modification. The molar fractions of major elements on the sulfidized cuprite surfaces with and without modification are shown in Table 3. After treatment with H_2O_2 , the molar fraction of Cu decreased from 28.08% to 26.27%. This reduction

could occur because cuprous oxide species on the cuprite surface were converted to copper oxide species after modification, resulting in a decrease in the relative content of Cu on cuprite. The molar fraction of S increased from 15.96% to 18.47% on the sulfide-treated cuprite surface after modification. This result indicated that modification with H₂O₂ could enhance the sulfidization of cuprite, resulting in an increase in the content of effective sulfur species on cuprite. These changes would create favorable conditions for subsequent interaction with the collector. Figure 14 shows the O 1s spectra of sulfidized cuprite surfaces with and without modification. After treatment with H₂O₂, the binding energies of O(II) species on the cuprite surface did not change significantly.

Figure 15 shows the Cu 2p spectra of the sulfidized cuprite surfaces with and without H_2O_2 modification. The binding energy of copper species

Table 3 Molar fractions of major elements on sulfidized cuprite surfaces treated with 1×10^{-3} mol/L Na₂S, and 5×10^{-4} mol/L H₂O₂ and 1×10^{-3} mol/L Na₂S

01.	Molar fraction/%			
Sample	O 1s	Cu 2p	S 2p	
Treated with Na ₂ S	55.96	28.08	15.96	
Treated with H_2O_2 and Na_2S	55.26	26.27	18.47	



Fig. 14 O 1s XPS spectra of cuprite surfaces: (a) Treated with 1×10^{-3} mol/L Na₂S; (b) Treated with 5×10^{-4} mol/L H₂O₂ and 1×10^{-3} mol/L Na₂S



Fig. 15 Cu 2p XPS spectra of cuprite surfaces: (a) Treated with 1×10^{-3} mol/L Na₂S; (b) Treated with 5×10^{-4} mol/L H₂O₂ and 1×10^{-3} mol/L Na₂S

on the cuprite surface did not change greatly after treatment with H₂O₂, and the observed small shifts in the binding energies may have been caused by a charging effect. Figure 16 shows the molar fractions of Cu(I) and Cu(II) species on the sulfidized cuprite surfaces with and without modification. After treatment with H_2O_2 , the molar fractions of Cu(I) and Cu(II) species decreased from 24.08% to 22.86% and 4.00% to 3.41%, respectively. In consideration of the results obtained for the molar fractions of major elements on the sulfidized cuprite surfaces with and without modification, the decrease in the molar fractions of Cu(I) and Cu(II) species may be caused by a decrease in the total content of Cu on the cuprite surface. Table 4 shows the proportions of Cu(I) and Cu(II) species among the total copper species on the sulfidized cuprite surfaces with and without modification. The proportion of Cu(I) species among the total copper species increased from 85.77% to 87.04% compared with that of non-modified sample. This result suggested that more Cu(II) species on the cuprite surface treated with H₂O₂ could interact with sulfur ions and were reduced to Cu(I) species than that on untreated cuprite surface. The increase in the proportion of Cu(I) species suggested that modification with H₂O₂ gave a Na₂S-modified cuprite surface that would be beneficial to the flotation.



Fig. 16 Molar fractions of copper species on Na_2S -treated cuprite and H_2O_2 - and Na_2S -treated cuprite

Table 4 Quantification of Cu 2p species on sulfidized cuprite surfaces treated with 1×10^{-3} mol/L Na₂S, and 5×10^{-4} mol/L H₂O₂ and 1×10^{-3} mol/L Na₂S

Sampla	Species	Cu 2p _{3/2} binding	Species
Sample		energy/eV	proportion/%
Treated with	Cu(I)	932.65	85.77
Na_2S	Cu(II)	934.20	14.23
Treated with	Cu(I)	932.60	87.04
H ₂ O ₂ and Na ₂ S	Cu(II)	934.33	12.96

Figure 17 shows the S 2p XPS spectra of sulfidized cuprite surfaces with and without modification. The peaks at 161.71, 163.98, and 168.44 eV were attributed to S^{2-} , S_n^{2-} , and SO_n^{2-} species on the cuprite surface, respectively [36]. After treatment with H₂O₂, the binding energy of SO_n^{2-} species on the sulfidized cuprite surface shifted to 168.29 eV. This shift suggested that the chemical state of the SO_n^{2-} species changed. Figure 18 shows the molar fractions of S^{2-} and S_n^{2-} species on sulfidized cuprite surfaces with and without modification. The molar fractions of S²⁻ and S_n^{2-} species increased from 12.81% to 15.10%, and 1.44% to 2.11% compared with non-modified, respectively. This indicated that modification using H₂O₂ before sulfidization could enhance the adsorption of sulfur ions on cuprite and increase the generation of hydrophobic copper sulfide species. Meanwhile, the increase in S_n^{2-} species may facilitate the floatability of cuprite through the generation of active $Cu-S_n$ species. Table 5 shows the proportions of S^{2-} , S_n^{2-} , and SO_n^{2-} species among the total S species on the sulfidized cuprite surfaces



Fig. 17 S 2p XPS spectra of cuprite surfaces: (a) Treated with 1×10^{-3} mol/L Na₂S; (b) Treated with 5×10^{-4} mol/L H₂O₂ and 1×10^{-3} mol/L Na₂S

with and without modification. The proportions of S^{2-} and S_n^{2-} species among the total S species increased from 80.29% to 81.75% and 9.00% to 11.42% compared with those of non-modified sample, respectively. These results suggested that more Cu-S and Cu-S_n species were generated on cuprite when it was treated with H2O2 before sulfidization. An increase in $Cu-S_n$ species is important for enhancing the hydrophobicity of cuprite because of the high activities of these species with collectors. In addition, the proportion of SO_n^{2-} species among the total S species decreased from 10.71% to 6.83% compared with nonmodified, which was favorable to the flotation of cuprite because of the hydrophilic characteristics of SO_n^{2-} and its compounds. The XPS results showed that the proportion of Cu(I) species among the total copper species and the molar fractions of S²⁻ and S_n^{2-} species on the sulfidized cuprite surfaces H_2O_2 treatment. increased with Therefore, modification with H₂O₂ could strengthen the sulfidization process of cuprite and promote the formation of copper sulfide species on the cuprite surface. This would enhance adsorption of the collector and the hydrophobicity of the cuprite surface, which would improve the conditions for sulfidization flotation of cuprite.



Fig. 18 Molar fractions of S species on surfaces of Na_2S -treated cuprite and H_2O_2 - and Na_2S -treated cuprite

Table 5 Quantification of S 2p species on sulfidizedcuprite surfaces treated with 1×10^{-3} mol/L Na2S, 5×10^{-4} mol/L H2O2 and 1×10^{-3} mol/L Na2S

Sample	Species	S 2p _{3/2} binding energy/eV	Species proportion/%
	S^{2-}	161.71	80.29
Treated with	S_{n}^{2-}	163.98	9.00
11025	SO_n^{2-}	168.44	10.71
Treated with	S^{2-}	161.70	81.75
H_2O_2 and	S_{n}^{2-}	163.84	11.42
Na_2S	SO_n^{2-}	168.29	6.83

3.2.7 Microflotation behavior

To confirm our earlier experimental results, we comprehensively investigated the effects of the oxidant, sulfurizing reagent, and collector doses on the flotation of cuprite. Sulfidization flotation tests of cuprite with different concentrations of H_2O_2 were carried out to study the influence of modification on cuprite sulfidization flotation (Fig. 19). During the sulfidization process, the pulp pH was adjusted to 9.5. Without modification, the recovery of the cuprite was 61.74% (Fig. 19), which indicated that the direct sulfidization flotation of cuprite was not ideal. When cuprite was oxidized with H₂O₂ before sulfidization, the flotation recovery of cuprite increased. When the H₂O₂ concentration was 5×10^{-5} mol/L, the flotation recovery of cuprite increased to 72.21%. When the H_2O_2 concentration was increased to 5×10^{-4} mol/L, the flotation recovery of cuprite reached 83.30%. These results showed that modification of the cuprite surface greatly improved the flotation



Fig. 19 Flotation recovery of cuprite as function of H_2O_2 concentration at 1×10^{-3} mol/L Na₂S, 5×10^{-4} mol/L NaBX, and pH 9.5

recovery of cuprite. However, with further increase in the H_2O_2 concentration, the flotation recovery of cuprite decreased. With 2×10^{-3} mol/L H₂O₂, the flotation recovery of cuprite was 76.88%. This decrease could be caused by the presence of residual oxidant in the pulp, which would consume Na₂S. As a result, it was difficult to sufficiently sulfidize the cuprite surface and the collector was not adsorbed stably on the mineral surface. The effect of the H₂O₂ concentration on the flotation results of cuprite showed that an appropriate dose of H₂O₂ was required to pre-oxidize the cuprite surface to improve the flotation behavior of cuprite. Excess H_2O_2 was not conducive to the sulfidization of cuprite and would be detrimental to the flotation environment for cuprite.

We also performed flotation tests of cuprite with changes in the NaBX concentration (Fig. 20) and Na_2S concentration (Fig. 21) in the absence and in the presence of H_2O_2 . Within the investigated concentration range of NaBX, the flotation recovery of pre-oxidized cuprite was obviously higher than that for the direct sulfidization flotation (Fig. 20). When the NaBX concentration was 4×10^{-4} mol/L, the flotation recovery of oxidant-treated cuprite was 74.48% and the recovery of cuprite without modification was 55.42%. When the NaBX concentration exceeded 5×10^{-4} mol/L, the flotation recovery of cuprite with and without modification plateaued. In the investigated concentration range for Na₂S, the floatability of modified cuprite was better than that of directly sulfidized cuprite (Fig. 21). However, when the concentration of Na_2S



Fig. 20 Flotation recovery of cuprite as function of NaBX concentration at 5×10^{-4} mol/L H₂O₂, 1×10^{-3} mol/L Na₂S, and pH 9.5



Fig. 21 Flotation recovery of cuprite as function of Na₂S concentration at 5×10^{-4} mol/L H₂O₂, 5×10^{-4} mol/L NaBX, and pH 9.5

exceeded 1×10^{-3} mol/L, an obvious downward trend was observed in the cuprite recovery. When the concentration of Na₂S was 5×10^{-3} mol/L, the recovery of directly sulfidized cuprite was only 27.86% and that of oxidant- and sulfide-treated cuprite was only 61.44%. These results could be caused by an excess of Na₂S, resulting in sulfur ions remaining in the pulp. Sulfur ions would compete with the collector for adsorption on the cuprite surface. In addition, the adsorption of excess sulfur ions on the mineral surface would give the surface a negative charge, which would not be conducive to adsorption of the anionic collector. The flotation results indicated that H₂O₂ treatment of cuprite was beneficial to the flotation. This was attributed to the fact that pre-oxidization of the cuprite surface could strengthen the adsorption of sulfur ions in the sulfidization process. The increased adsorption would ensure that the surface of cuprite was sufficiently sulfidized to promote the adsorption of xanthate and enhance the hydrophobicity of the cuprite surface.

Figure 22 shows a schematic diagram of the mechanism of enhanced sulfidization of cuprite after modification with H_2O_2 . It is difficult to obtain fully sulfidized cuprite surfaces by direct sulfidization. However, after modification of the cuprite surface with H_2O_2 , the copper species on the surface change from Cu(I) to Cu(II), which has stronger affinity than Cu(I) for sulfur ions. This greatly enhances the sulfidization of cuprite. The surface of the modified cuprite can react strongly



Fig. 22 Schematic diagram of surface-enhanced sulfidization mechanism of cuprite via modification with H_2O_2 and its response to xanthate adsorption and flotation

with xanthate after sulfidization, which significantly enhances the floatability of cuprite. These results will be very important for realizing efficient and clean recovery and utilization of copper oxide ores from cuprite in industry.

4 Conclusions

(1) Modification using H_2O_2 increased the amount of NaBX adsorbed on the cuprite surface.

(2) More Cu–S and Cu–S_n species were generated on the cuprite surface after modification with H_2O_2 .

(3) The flotation recovery of cuprite modified with H_2O_2 was obviously higher than that obtained after direct sulfidization flotation.

(4) Modification with H_2O_2 could enhance the sulfidization of cuprite and provide a Na₂Smodified cuprite surface that is beneficial to the flotation.

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过氧化氢表面改性强化硫化浮选赤铜矿

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摘 要:使用过氧化氢作为氧化剂对赤铜矿表面进行改性处理以实现赤铜矿的强化硫化。表面吸附和红外光谱实验结果表明,硫化前使用过氧化氢对赤铜矿表面进行改性可增加黄药在赤铜矿表面的吸附量。Zeta 电位、扫描电子显微镜、X 射线光电子能谱和飞行时间二次离子质谱实验结果表明,经过氧化氢改性后的赤铜矿表面生成了更多的 S²⁻和 S_n²⁻组分。微浮选实验结果表明,经过氧化氢改性后的赤铜矿浮选回收率从 61.74%增加到 83.30%。微浮选实验与表面测试分析结果证实,过氧化氢对赤铜矿表面的改性处理能增强赤铜矿表面的硫化过程,从而改善赤铜矿的浮选行为。

关键词:赤铜矿;浮选;过氧化氢;表面改性;硫化

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